UNITED STATES DEPARTMENT OF COMMERCE
JESSE H. JONES, Secretary
NATIONAL BUREAU OF STANDARDS
Lyman J. Briggs, Director

✦

Journal of Research

of the

National Bureau of Standards

✦

Volume 29, Number 5
November 1942

[Published with approval of the Director of the Budget]

UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON : 1942

For sale by the Superintendent of Documents, Washington, D. C. - - - - - - Price 30 cents
$3.50 per year on subscription

The prices of the separate Research Papers appearing in this JOURNAL are given on the front cover page. If 100 or more copies of any separate are ordered, a discount of 25 percent is allowed. Those who desire copies of separate Research Papers should send their orders and remittances without delay to the Superintendent of Documents, U. S. Government Printing Office, Washington, D. C. This will aid him to determine the number of copies to be printed for sale. Research Papers are not printed from electrotypes, and usually no more reprints can be had when the first and only printing is exhausted.

MATHEMATICAL TABLES

A list of the mathematical tables now obtainable from the National Bureau of Standards is printed on pages 3 and 4 of the JOURNAL cover. New tables will be announced from time to time as they become available.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1502

Part of Journal of Research of the National Bureau of Standards, Volume 29, November 1942

A REEXAMINATION OF THE POTSDAM ABSOLUTE DETERMINATION OF GRAVITY

By Hugh L. Dryden

ABSTRACT

Recent absolute determinations of the acceleration of gravity differ from the generally accepted Potsdam value by amounts considerably greater than the probable error assigned to that value by the Potsdam investigators. The discrepancy is due in large part to an adjustment made with the intent of correcting for certain systematic errors. The adjustment was probably not warranted. If this adjustment is not made, the Potsdam result is about 12 parts per million less than the commonly accepted value as compared with 14 and 20 parts per million less as found in the recent absolute determinations. The best value of g for general use when accurate absolute values are needed is probably obtained by reducing the local value in the Potsdam system by about 15 parts per million. The Subcommittee on Gravity of the National Research Council Committee on Fundamental Physical Constants has recommended a reduction of 17 parts per million.

CONTENTS

	Page
I. Introduction	303
II. The Potsdam pendulums	304
III. Observed results	305
IV. The final adjustment	311
V. Suggested revision of Potsdam value	314
VI. Best value of g	314

I. INTRODUCTION

The present accepted international base for gravity measurements is Potsdam, Germany. The value of gravity for the base station, 981.274 cm/sec^2, is the result of an absolute determination by F. Kühnen and Ph. Furtwängler, whose observations are described in great detail in a 1906 publication of the Königliche Preussische Geödatische Institut entitled "Bestimmung der absoluten Grösse der Schwerkraft zu Potsdam mit Reversionspendeln." The completeness of the investigation and of the report, which includes a discussion of all the suggested sources of accidental and systematic error, has won universal acceptance for this value.

However, recent determinations indicate that the Potsdam value is too large. Thus, in 1936, Paul R. Heyl and Guy S. Cook published [1] the results of an absolute determination at Washington, also made with reversible pendulums, which gave a result 0.020 cm/sec^2 (20 parts per million) lower than the value derived from the Potsdam

[1] J. Research NBS **17**, 805 (1936) RP946.

value by means of a direct connection between the two stations made in 1933 [2] by E. J. Brown, of the United States Coast and Geodetic Survey.

In 1939 [3] J. S. Clark published the results of an absolute determination at the National Physical Laboratory, Teddington, England, again made with a reversible pendulum, which gave a result 0.013_8 cm/sec^2 (14 parts per million) lower than the value derived from the Potsdam value and a number of transfer measurements adjusted by E. C. Bullard and H. L. P. Jolly.[4]

Relative measurements between Teddington and Washington have recently been made by B. C. Browne and E. C. Bullard.[5] These relative measurements gave a difference between the acceleration of gravity at Teddington and Washington of 1.096_9 cm/sec^2, whereas the difference between the absolute measurements was 1.101_5 cm/sec^2, that is, agreement within 4.6 parts per million. Browne and Bullard conclude that there is "little doubt that the hitherto accepted value at Potsdam is some seventeen parts in a million too great" and that "this correction should be applied to values in the Potsdam system when values of g are to be used in connection with other physical quantities (for example in the determination of the electrical units.)"

The present paper summarizes the result of a study of the Potsdam determination made at the time that Heyl and Cook's paper was under editorial review. It is now published in view of interest in the selection of the "best" value of g for use in the work of the National Research Council Committee on Fundamental Physical Constants. The reexamination of the Potsdam result shows that the value obtained after correction for known effects was 11.8 parts per million lower than that finally given, the mean value having been changed by this amount as a result of a procedure intended to correct for certain types of systematic errors. There is some doubt as to the effectiveness of this procedure.

There is great need of an absolute determination by some other method than that of the reversible pendulum to determine definitely the magnitude of the systematic errors present in the measurements with reversible pendulums. Under present world conditions, however, other scientific problems are much more urgent, and this one must await more normal times.

II. THE POTSDAM PENDULUMS

Five pendulums were used by Kühnen and Furtwängler, each consisting of a tube with a heavy solid cylindrical weight on one end and a light hollow weight of the same external shape and dimensions on the other end. The lengths of the tubes were between 1,116 and 1,125 mm; the external diameters were between 41 and 44 mm; and the wall thicknesses were between 1 and 2 mm. The five pendulums were designated as follows: Light Austrian (mass, 2.86 kg); Geodetic Institute (mass, 5.57 kg); Italian (mass, 5.87 kg); Heavy Austrian (mass, 6.23 kg); Half-second (mass. 3.53 kg). The first four were seconds pendulums, so that the distance between the two axes of

---

[2] U. S. Coast and Geodetic Survey, Spec. Pub. No. 204 (1936).
[3] Phil. Trans. Roy. Soc. (London) [A] **238**, 65–123 (1939).
[4] Monthly Notices Roy. Astron. Soc., Geophys. Suppl. **3**, 443–477 (1935) and **4**, 132 (1937).
[5] Proc. Roy. Soc. (London) [A] **175**, 110 (1940).

rotation was about 100 cm; the last was a half-second pendulum with distance between axes of 24.9 cm.

Each pendulum could be swung on one or more pairs of knife edges fastened to the pendulum, the knife edges resting on planes fixed to the support; or it could be swung on planes fastened to the pendulum, the knife edges being fixed to the support. One pair of knife edges could be used for all five pendulums; these are accordingly designated "universal." In addition, each pendulum had a pair of knife edges; these are designated "own." The two Austrian pendulums used the same pair.

In all the pendulums the knife edges could be removed and interchanged in position, and for all except the light Austrian pendulum, the weights could be interchanged.

With knife edges mounted in the pendulum, the supporting planes were either two agate stones mounted in a small bridgelike support on which all five pendulums could be swung or a larger support intended mainly for the three heaviest pendulums. These supports are designated "small bridge" and "large bridge," respectively.

The measurements on the pendulums with knife edges were made in air at atmospheric pressure; those on the pendulums with planes were made in an evacuated cylinder at pressures from 20 to 760 mm mercury.

III. OBSERVED RESULTS

The procedure followed in the observations may be reviewed briefly as follows: A series of observations on a given pendulum with a given method of support usually occupied 4 days. On the first day, the period was measured first with heavy weight below and then with heavy weight above (i. e. with the pendulum rotated about a horizontal axis, or "reversed"). The pendulum was then rotated about a vertical axis, and the period measured first with heavy weight above and then with heavy weight below. On the second day, the distance between the knife edges was measured for each of the four positions, and the distance of the center of gravity from the knife edges determined. The weights or knife edges were then removed from the pendulum and interchanged. On the third day, length measurements and the center-of-gravity determination were made, and on the fourth day, periods for the four positions were measured as on the first day. Frequently the order was changed to give length measurements on the first and fourth days.

From such a normal series of eight times of swing, four values of the length of the simple seconds pendulum were computed, that is, each sequence of swings with heavy weight above and below was treated independently. Corrections were applied to each individual time of swing for amplitude and damping, for temperature, for vertical temperature gradient, for difference in air density between swings in upright and reversed positions, for clock rate, and, when the planes were fixed in the pendulum, for the angle of inclination between the planes. The apparent length of the simple seconds pendulum was then computed for each pair of times of swing. To these values were applied corrections for the motion of the pendulum support, for flexure of the pendulum, for extension of the pendulum under load, and for asymmetry. There resulted 192 values for the length of the simple seconds pendulum, which are given in full in table 1. The

magnitude of the corrections, which have been applied to the observed values to obtain the values given in table 1, is indicated in table 2.

TABLE 1.—*Potsdam values of length of seconds pendulum after correction for known effects but before final adjustment for unknown systematic errors* [a]

Bearing [b]	Bridge [c]	Change between determinations [d]	Length of a seconds pendulum from observations, corrected (10^{-7} meter)	First average	Second average
Light Austrian pendulum; mass, 2.86 kg					
O	*L*		9943152	9942337	9942330
O	*L*	*K*	1521		
O	*L*	*R*	3198	2324	
O	*L*	*K*	1450		
U	*S*		2374	2373	
U	*S*	*K*	2332		
U	*S*	*R*	2336	2365	
U	*S*	*K*	2395		
U	*S*	*A*	2318	2372	
U	*S*	*K*	2426		
U	*S*	*R*	2377	2402	
U	*S*	*K*	2427		
P			2241	2341	2346
P			2441		
P			2299	2358 [b]	
P			2418		
P			2252	2337 [b]	
P			2423		
Geodetic Institute pendulum; mass, 5.57 kg					
O	*S*		9942341	9942294	9942291
O	*S*	*W*	2246		
O	*S*	*R*	2254	2228	
O	*S*	*W*	2201		
O	*S*	*D*	2267	2261	2261
O	*S*	*W*	2255		
O	*S*	*R*	2242	2261	
O	*S*	*W*	2281		
O	*S*	*D*	2282	2238	2263
O	*S*	*W*	2193		
O	*S*	*R*	2361	2292	
O	*S*	*W*	2223		
U	*S*		2379	2236	2264
U	*S*	*W*	2093		
U	*S*	*R*	2377	2293	
U	*S*	*W*	2209		
U	*L*		2292	2320	2334
U	*L*	*W*	2349		
U	*L*	*R*	2215	2348	
U	*L*	*W*	2480		
O	*L*		2123	2257	2250
O	*L*	*W*	2391		
O	*L*	*R*	2111	2242	
O	*L*	*W*	2373		
P			2323	2292 [b]	2323
P			2262		
P			2355	2354	
P			2353		
P			2270	2253	2262
P			2236		
P			2262	2241	
P			2220		
P			2276	2260 [b]	
P			2245		

See footnotes at end of table.

TABLE 1.—*Potsdam values of length of seconds pendulum after correction for known effects but before final adjustment for unknown systematic errors* [a]—Continued

Bearing [b]	Bridge [c]	Change between determinations [d]	Length of a seconds pendulum from observations, corrected (10^{-7} meter)	First average	Second average
Italian pendulum; mass, 5.87 kg					
0	S		9942435	9942299	9942289
0	S	W	2163		
0	S	R	2381	2279	
0	S	W	2178		
0	S	K	2361	2245	2259
0	S	W	2129		
0	S	R	2448	2274	
0	S	W	2101		
0	S	K	2432	2267	2283
0	S	W	2102		
0	S	R	2458	2300	
0	S	W	2143		
0	S	K	2425	2268	2250
0	S	W	2112		
0	S	R	2405	2232	
0	S	W	2059		
0	S	K	2405	2234	2228
0	S	W	2062		
0	S	R	2372	2222	
0	S	W	2072		
0	S	K	2374	2208	2221
0	S	W	2042		
0	S	R	2437	2234	
0	S	W	2032		
0	S	K	2238	2170	2156
0	S	W	2102		
0	S	R	2224	2142	
0	S	W	2059		
0	S	K	2402	2218	2242
0	S	W	2035		
0	S	R	2469	2267	
0	S	W	2066		
0	L		2184	2315	2304
0	L	W	2446		
0	L	R	2122	2294	
0	L	W	2466		
U	S		2029	2194	2222
U	S	W	2360		
U	S	R	2112	2249	
U	S	W	2387		
P			2171	2191[b]	2216
P			2212		
P			2203	2230[b]	
P			2258		
P			2178	2226	
P			2274		
P			2210	2251[b]	2249
P			2293		
P			2188	2247	
P			2306		
P			1969	2191	2190
P			1979		
P			2408		
P			1954	2191	
P			1978		
P			2416		
P			2001	2197	
P			1959		
P			2414		
P			1975	2179	
P			1983		
P			2380		

See footnotes at end of table.

TABLE 1.—*Potsdam values of length of seconds pendulum after correction for known effects but before final adjustment for unknown systematic errors* [a]—Continued

Bearing [b]	Bridge [c]	Change between determinations [d]	Length of a seconds pendulum from observations, corrected (10^{-7} meter)	First average	Second average
Italian pendulum; mass, 5.87 kg.—Continued					
P			9941979		
P			1975		
P			2275	9942144	
P			2348		9942130
P			1977		
P			2257	2117	
Heavy Austrian pendulum; mass, 6.23 kg					
O	*L*		9941701		
O	*L*	*W*	2983	9942342	
O	*L*	*R*	1752		9942350
O	*L*	*W*	2963	2358	
U	*S*		2152		
U	*S*	*W*	2226	2189	
U	*S*	*R*	2177		2215
U	*S*	*W*	2305	2241	
P			2198		
P			2258	2228	
P			2206		
P			2282	2244	2232
P			2196		
P			2253	2224 [g]	
Half-second pendulum; mass, 3.53 kg					
O	*S*		9942154		
O	*S*	*W*	2519	9942337	
O	*S*	*R*	2132		9942333
O	*S*	*W*	2525	2329	
O	*S*	*R*	2109		
O	*S*	*W*	2479	2294	
O	*S*	*R*	2080		2290
O	*S*	*W*	2491	2286	
Half-second pendulum—weights removed and replaced					
O	*S*		9942575		
O	*S*	*W*	2180	9942378	
O	*S*	*R*	2557		9942358
O	*S*	*W*	2122	2339	
O	*S*	*R*	2458		
O	*S*	*W*	2160	2309	
O	*S*	*R*	2500		2322
O	*S*	*W*	2172	2336	
U	*S*		2274		
U	*S*	*R*	2223	2249	
U	*S*	*A*	2329		
U	*S*	*R*	2168	2249	
U	*S*	*W*	2349		2262
U	*S*	*R*	2227	2288	
U	*S*	*A*	2397		
U	*S*	*R*	2128	2262	
P			1960		
P			2040	2000	
P			1978		
P			2151	2014 [g]	2002
P			1956		
P			2029	1992 [g]	

See footnotes at end of table.

TABLE 1.—*Potsdam values of length of seconds pendulum after correction for known effects but before final adjustment for unknown systematic errors* [a]—Continued

Bearing [b]	Bridge [c]	Change between determinations [d]	Length of a seconds pendulum from observations, corrected (10^{-7} meter)	First average	Second average
Half-second pendulum—weights removed and replaced—Continued					
P			9941493	9941918$_5$	
P			2344		
P			1499	1921$_5$	9941919
P			2344		
P			1503	1917	
P			2331		
P			1195	1971	
P			2747		1971
P			1216	1971	
P			2726		
P			1201	1814	
P			2427		1817
P			1192	1820	
P			2448		
P			1474		
P			1671	1933	
P			2293		1890
P			1591		
P			1848	1848	
P			1976		
P			2324	1947	
P			1570		1974
P			2508	2001$_5$	
P			1495		
P			2160	2047$_5$	
P			1935		2062
P			1725	2076$_5$	
P			2427		

[a] This table recapitulates the values given in columns 18 and 19 of table 9, p. 216–233, and columns 19 and 20 of table 13, p. 303–315, of Kühnen and Furtwängler's report, rearranged to bring together the values for a given pendulum.

[b] *O*=own knife edges, *U*=universal knife edges, *P*=planes.

[c] *L*=large bridge, *S*=small bridge.

[d] This column gives change made since preceding run.
R=pendulum rotated about vertical axis.
K=knife edges interchanged.
W=weights interchanged.
A=change in amplitude.
D=change in azimuth of plane of vibration.

TABLE 2.—*Magnitude of corrections applied by Kühnen and Furtwängler for known effects*

Source of correction	Magnitude (parts in 10^7)
Amplitude and damping	−30 to −1
Temperature	−196 to +129
Vertical temperature gradient	−2 to +1
Air density	−182 to +385
Clock rate	−615 to +40
Angle of inclination of planes	−11 to +21

	Light Austrian	Geodetic Institute	Italian	Heavy Austrian	Half-second
Motion of support	14	27	28	30	69
Flexure	−48	−37	−47	−41	20
Extension under load	11	15	11	13	7
Asymmetry, heavy weight below	32	9	−118	−13	−64
Asymmetry, heavy weight above	32	−48	−91	10	40

No attempt will be made to discuss the details of these corrections. Amplitude and damping corrections are by well-known formulas; they amount at most to 3 parts per million. The temperature correction relates to the thermal expansion of the pendulum; the values depend on the reference temperature selected and for the majority of the observations were only a few parts per million, much less than the maximum values given in table 2. The correction for vertical temperature gradient did not exceed 2 parts in 10 million. Except in a few series no air-density correction was required in the measurements with knife edges. In the measurements with planes, the corresponding times of swing were not usually consecutive; hence the air densities were slightly different, and a reduction to the same density was required. The constants required were determined by observations at different densities. The clock-rate correction is self-explanatory. The correction for inclination of the planes in the measurements with planes amounted to 1 or 2 parts per million.

The correction for motion of support was determined experimentally. The flexure and extension corrections were computed by well-known formulas. The correction for asymmetry relates to the effect of the air on the motion of the pendulum. When working in air at atmospheric pressure, the effect of the air will not cancel for the two positions of the pendulum unless the pendulum is perfectly symmetrical. The corrections were computed from observations on each pendulum at different air pressures.

The interchange of weights reverses the sign of the error produced by the finite radius of curvature of the knife edges, and hence Kühnen and Furtwängler took averages of pairs of values with weights interchanged. In the case of the light Austrian pendulum, where an interchange of weights was not possible, the knife edges were interchanged; this reduces but does not completely eliminate the error. These average values are listed in table 1 as "first average." Because of rearrangement of the observations, table 1 indicates a greater number of weight and knife-edge interchanges than were actually made. As previously stated, observations with the pendulum rotated about a vertical axis were usually made before the interchange of weights.

Those observations made in the same series of (usually) 4 days were then averaged to give 40 values, which are designated "second average" in table 1. *These values Kühnen and Furtwängler consider of equal weight.* They range from 9941817 to $9942373\times10^{-7}\ m$, the maximum difference being 56 parts per million. These 40 values were next subjected to a least-squares adjustment described in the next section, which gave an adjusted value of $9942380\times10^{-7}\ m$, higher than any one of the 40 values.

Before discussing this adjustment, it is of interest to consider the relation between various weighted mean values of the data given in table 1 to the adjusted value. Various mean values are given in table 3, together with the average deviation of the individual observations from the mean.

The mean values for each pendulum with knife edges and with planes agree within 5 parts per million except for the half-second pendulum, for which the values differ by 35 parts per million. The average deviation of any single observation from the mean for a given pendulum and support varies from 1 to 7 parts per million. Various

methods of weighting give mean values which are from 12 to 17 parts per million lower than the final adjusted value.

TABLE 3.—*Comparison of various mean values with final adjusted value given by Kühnen and Furtwängler*

Pendulum	Support	Mean value	Number of observations	Average deviation from mean	Amount below final adjusted value [a]
Light Austrian, *A*	Knife edges	9942359	6	21	21
	Planes	2346	3	9	34
Geodetic Institute, *B*	Knife edges	2273	12	31	107
	Planes	2280	5	34	100
Italian, *C*	Knife edges	2246	20	35	134
	Planes	2197	11	31	183
Heavy Austrian, *D*	Knife edges	2283	4	68	97
	Planes	2232	3	8	148
Half-second, *E*	Knife edges	2305	12	33	75
	Planes	1950	16	60	430
BCD		2247	55	39	133
ABCD		2262	64	49	118
All, 92 first averages of table 1 given equal weight		2213	92	102	167
All, mean values for each pendulum given equal weight		2244	(5)	63	136
All, values for 18 pendulum and support combinations given equal weight		2263	(18)	60	117
All, values of 40 second averages of table 1 given equal weight		2212	(40)	98	168

[a] The final adjusted value is 9942380, to which a correction of +10 is applied for the effect on the length measurements of the rising temperature produced by the presence of the observers. The result is given as $L=994.239\pm0.003$, from which $g=981.274\pm0.003$ cm/sec^2 at Potsdam.

IV. THE FINAL ADJUSTMENT

The final adjustment was intended to correct for systematic errors arising from the deformation of the knife edges and planes and other departures from the assumed conditions of infinitely small frictionless swinging of the pendulum about a fixed axis of rotation.

The first source of error discussed is that arising from the finite radius of curvature of the knife edge, the contact being assumed to be a rolling contact between a cylinder and plane or between two cylinders. Systematic errors from this source are eliminated by interchanging the weights or knife edges when the knife edges are mounted in the pendulum and are negligible when planes are mounted in the pendulum.

The second type of contact discussed is that in which the knife edge of finite radius makes a cylindrical depression in the supporting plane and slips as the pendulum swings, as if rotating in a cylindrical bearing. The error from this source is shown to be inversely proportional to the distance between the knife edges.

The third type of contact is the same as the preceding except that under the lateral load arising from the reaction at the support, the knife edge is assumed to bend elastically and the contact area of the plane is also assumed to deform laterally. The effect is in general the same as that of motion of the pendulum support, except that it can not be detected by the usual method of measuring the motion of the support. The error from this source consists of two terms, one inversely proportional to the distance between knife edges, the second directly proportional to the mass and inversely proportional to the distance between knife edges.

Systematic errors of this form are undoubtedly present. *Kühnen and Furtwängler assume that their observations are sufficiently numerous*

and accurate to determine the magnitude of these errors from the observations on the different pendulums which vary in mass and distance between knife edges. Tacitly it is also assumed that systematic errors which do not vary with the mass and distance between knife edges have the characteristics of accidental errors.

The following steps are straightforward. It is assumed that the adjusted value L is given by the formula

$$L=L'+\frac{q}{\Lambda}+\frac{M}{\Lambda}p,$$

in which L' is the value corrected for known effects (the second average values in table 1), Λ is the distance between knife edges, M the mass, and p and q are unknown coefficients to be determined from the observations. Forty observation equations are set up, normal equations formed and solved. Any reasonable combination of results gives a correction of 10 to 17 parts per million to be added to the mean value. The results give a practically constant value of p for all conditions of support of 30, a value of q for knife edges in the pendulum of -82, and a value of q for planes in the pendulum of -9, L being in units of 10^{-7} meter. The effect of the adjustment is shown in table 4.

TABLE 4.—*Effect of final adjustment on values for individual pendulums*

Pendulum	Support	Mean value before adjustment	Deviation from mean of all before adjustment	p correction	q correction	Mean value after adjustment	Deviation from mean of all after adjustment
Light Austrian	Knife edges	9942359	112	86	−82	9942363	−19
	Planes	2346	99	86	−9	2423	41
Geodetic Institute	Knife edges	2273	26	167	−82	2358	−24
	Planes	2280	33	167	−9	2438	56
Italian	Knife edges	2246	−1	176	−82	2340	−42
	Planes	2197	−50	176	−9	2364	−18
Heavy Austrian	Knife edges	2283	36	187	−82	2388	6
	Planes	2232	−15	187	−9	2410	28
Half-second	Knife edges	2305	58	424	−328	2401	19
	Planes	1950	−97	424	−36	2338	−44
	Average	[a] 2247	53			[a] 2382	31

[a] These values differ from those in table 3 and from Kühen and Furtwängler's adjusted mean value by 2 or 3 parts in 10^{-7}, because here each pendulum is given equal weight, whereas, in the other places each determination is given the same weight.

the assumptions underlying the adjustment are granted, no fault can be found with the details of the adjustment. Kühnen and Furtwängler point out the very uneven contribution of the various pendulums to the final values. Thus observations on the half-second pendulum do not enter at all into the determination of p, although the largest p correction is applied to that pendulum. The final value of L is determined largely by the results on the light Austrian pendulum (9 out of 92 observations). The final result is equivalent to taking the weighted mean for the results of all the pendulums when the following weights have been assigned: Light Austrian, 1.00; half-second, 0.33; Geodetic Institute, 0.20; Italian, 0.11; heavy Austrian, 0.003.

The p term arises from the lateral motion of the axis of rotation produced by bending of the knife edge and the lateral distortion of the contact area of the plane. It is of the same nature as the lateral motion of the pendulum support for which the correction was determined experimentally. The least-squares adjustment gives a p correction six times that made for motion of the pendulum support, which would mean lateral motions due to the deformation six times as great as those of the support as a whole.

W. R. Osgood, of this Bureau, has computed the bending of the knife edge on the basis of the theory of elasticity and concludes that it is highly improbable that the effect of bending of the knife edge could amount to as much as 1 part in a million in the value of the length of the seconds pendulum.

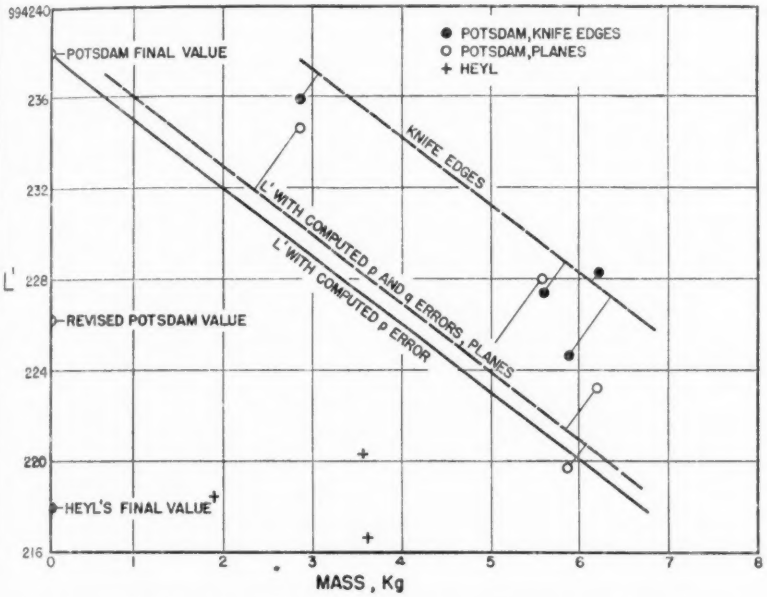


FIGURE 1.—*Potsdam final adjustment interpreted as extrapolation to zero mass.*

As stated previously, the observations with the half-second pendulum have no influence on the computation of the p correction. We may then regard the p correction as amounting to an extrapolation of the observed values on pendulums of the same length, which appear to vary with the mass, to a pendulum of zero mass. Figure 1 shows the mean values listed in table 4 plotted against the mass, and the p correction. In this figure are also plotted Heyl's values, which do not indicate a systematic variation with mass, though admittedly the same range of pendulum weight was not studied.

In the light of the more recent determinations and the preceding discussion, doubt is cast on the validity of the adjustment. Kühnen and Furtwängler in their discussion of the adjustment suggest that "if different reversible pendulums are to serve in the most favorable way for a determination of gravity, one must determine in advance of

the manufacture of the pendulums the masses and knife edge distances according to formula 131." This suggestion was not adopted by the later workers.

V. SUGGESTED REVISION OF POTSDAM VALUE

It is suggested that the systematic errors present in the individual Potsdam determinations arose from other causes than those discussed and that in the absence of further knowledge they should be considered of a random nature. From the good consistency of observations in any given pendulum-support combination, it is probable that the systematic errors depend on these combinations alone, being reasonably constant for any given combination. The mean values for each of the 18 combinations should then be given equal weight, which, as indicated in table 3, gives a value 11.7 parts per million less than that adopted by Kühnen and Furtwängler.

If the 92 first averages or the 40 second averages are given equal weight, the mean value is 16.7 or 16.8 parts per million less. The author feels that such weighting gives undue weight to the very low value obtained on the half-second pendulum with planes, to which 16 of the 92 or 7 of the 40 values apply.

VI. BEST VALUE OF g

The available absolute determinations become with this revision as follows, referred to the internationally accepted value:

Potsdam (revised)	−11.7 parts per million.
Heyl	−20.0 parts per million.
Clark	−13.8 parts per million.

The average is −15.2 parts per million. The best value of g for use when accurate absolute values are needed is probably obtained by reducing the value in the Potsdam system by about 15 parts per million.

The application of this procedure to Washington would give a value at the National Bureau of Standards base station, using Brown's transfer, of 980.085 cm/sec². However, since transfer measurements involve some uncertainties and one of the absolute determinations was made at Washington, it is perhaps better in this case to consider the following values:

Heyl's absolute determination	980.080
Clark's determination with Browne and Bullard's transfer	980.084_6
Potsdam determination (revised) with Brown's transfer	980.088_3

Giving the absolute determination made on the spot twice the weight of the other two, a value of 980.083 is obtained. This is believed to be a somewhat better value for use in connection with the absolute electrical measurements made at the National Bureau of Standards.

The Subcommittee on Gravity of the National Research Council Committee on Fundamental Physical Constants by somewhat different reasoning has recommended a reduction of values in the Potsdam system by 17 parts per million, corresponding to 980.083 at Heyl's station, in those cases where the most precise absolute values are desired.

WASHINGTON, October 29, 1941.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1503

Part of Journal of Research of the National Bureau of Standards, Volume 29, November 1942

CATALYZED HYDROLYSIS OF AMIDE AND PEPTIDE BONDS IN PROTEINS [1]

By Jacinto Steinhardt and Charles H. Fugitt [2]

ABSTRACT

The rates of hydrolysis by dilute acids of both a dissolved protein (egg albumin) and an insoluble protein (wool) are shown to depend not only on the temperature and acidity but also on the acid used. When hydrolyzed at 65° C by certain strong monobasic acids of high molecular weight, the amide and the peptide bonds are broken over 100 times as fast as when they are hydrolyzed with hydrochloric acid. Even among the common mineral acids, large differences appear. These differences in hydrolytic effectiveness parallel differences in the affinities of the anions of the acids for protein. A further reason for attributing this effect to the anions is the attainment, with anions of high affinity, of a maximum rate of amide hydrolysis at relatively low concentrations, stoichiometrically equivalent to the sum of the amino plus the amide groups. A similar limiting anion concentration or maximum rate of hydrolysis of the much more numerous peptide groups is not observed. On the basis of details of the dependence of the rate of hydrolysis on concentration of effective anions and hydrogen ions, a mechanism which involves combination of the groups hydrolyzed with hydrogen ions, is proposed.

At low concentrations of effective anions, amide hydrolysis is catalyzed more strongly than peptide hydrolysis. By keeping the concentration slightly below stoichiometric equivalence to the sum of the amino plus amide groups the amide groups may be rapidly hydrolyzed without extensive hydrolysis of the peptide bonds in the protein. Practical applications are suggested.

CONTENTS

	Page
I. Introduction	316
II. Experimental procedure	316
1. Experimental conditions	316
2. Analytical methods	316
III. Results and discussion	317
1. Relative effectiveness of different acids	317
2. Dependence of reaction rate on concentration of catalytically effective anions	319
3. Dependence of reaction rate on concentration of hydrogen ions	320
4. Dependence of reaction rate on concentration of effective anions and on temperature at higher concentrations of acid	321
5. Results obtained with a soluble protein	323
IV. Mechanism of the catalysis	324
V. Potential fields of application	326
VI. References	327

[1] A brief account of this work was presented at the Boston meeting of the American Society of Biological Chemists in April 1942.

[2] Research Associates at the National Bureau of Standards, representing the Textile Foundation.

I. INTRODUCTION

The rate of hydrolysis of proteins in dilute solutions of strong acids has long been known to depend on temperature and on concentration of acid. Recently it has been found that the rates of hydrolysis of both an insoluble protein (wool) and a soluble protein (egg albumin) also depend on the choice of hydrolyzing acid [7].[3] Since large differences in hydrolytic effectiveness appear among acids which are totally dissociated, it is evident that the rate of hydrolysis is influenced strongly by anions. This catalytic influence is further demonstrated by other experiments described in the present paper. The results yield information concerning the mechanism of hydrolysis, and suggest that proteins can be hydrolyzed under conditions considerably milder than those customarily employed.

II. EXPERIMENTAL PROCEDURE

1. EXPERIMENTAL CONDITIONS

Two proteins, purified wool and crystallized egg albumin, were hydrolyzed at two temperatures (65° C and 75° C, ±0.1°). Details of the purification of both proteins and, with few exceptions,[4] of the reagents used, have been described elsewhere [8, 9]. The kinetic procedures were as follows:

For each measurement with wool a portion was immersed in a quantity of solution, previously brought to the temperature of the thermostat. The proportion of 98 ml of solution per g of dry wool was always employed. With egg albumin, the concentration of protein, after mixing a stock solution with the reagents, was 0.71 percent. Glass-stoppered flasks were used; they were sealed as soon as the wool was thoroughly wetted, to prevent evaporation. After the desired time had elapsed, the flasks were cooled rapidly, opened, and aliquots of 5 or 10 ml were removed and analyzed as described in the next section.

Although the egg albumin is almost instantly denatured at the concentration of acid (0.053 *M*) used in the experiments with this protein, it remains in solution at all concentrations of sodium dodecylsulfonate above 0.01 *M*. However, as the products of hydrolysis accumulate, they precipitate, unless the concentration of dodecylsulfonate is above 0.016 *M*.

2. ANALYTICAL METHODS

A distinction has been made experimentally between the hydrolysis of amide bonds ($RCO\text{-}NH_2$) and of peptide bonds ($RCO\text{-}NHR'$). The first may be followed with both proteins by measuring the evolution of ammonia, whereas the second may be studied by a direct method (the formol titration) only with the soluble protein. However, other methods which indicate the extent of peptide hydrolysis are available, and were used with both proteins, as described later.

The ammonia evolved was adsorbed on permutit before distillation to remove it from much of the other dissolved material present, thus decreasing the danger of secondary production of ammonia during the

[3] Figures in brackets indicate the literature references at the end of this paper.

[4] The sulfate half-esters ($ROSO_3H$) were supplied through the courtesy of E. I. du Pont de Nemours & Co., Inc. Mixtures of these half-esters have been used to denature proteins [1].

distillation with alkali. In the experiments with egg albumin, determinations of ammonia were also made on protein-free filtrates, which were obtained by precipitating the unchanged protein with trichloroacetic acid as explained below. The results obtained by the two methods agreed closely.

The hydrolysis of peptide bonds in egg albumin was measured by determining the increase in the formol titration value, as in Northrop's modification [4] of Sörensen's method. Since the increase corresponds to the number of carboxyl groups liberated by the hydrolysis of both amide and peptide groups, the amount of hydrolysis of the latter is given by the difference between the increase in the formol titer and the amount of ammonia evolved.

As its peptide bonds are hydrolyzed, part of the wool dissolves. The amount dissolved, expressed in terms of its nitrogen content as determined by Kjeldahl analysis, has therefore been used as a convenient measure of the total extent of hydrolysis of the wool. Subtraction of the ammonia evolved gives a quantity designated as "nonammonia nitrogen," which depends only on the hydrolysis of peptide bonds. Since partially hydrolyzed egg albumin is not precipitated by trichloroacetic acid, Kjeldahl analyses of the solutions of this protein, after mixing with trichloroacetic acid, have been used as an additional indication of the extent of peptide hydrolysis in this protein. The term "dissolved nitrogen" is also applied to this experimental quantity.

The presence of sodium dodecylsulfonate and certain other salts interfers with the precipitation of protein by trichloroacetic acid in the concentrations of this reagent customarily used. However, tests showed that in the presence of 0.03 *M* sodium dodecylsulfonate, the amount of protein precipitated was practically independent of the concentration of trichloroacetic acid at concentrations above 0.47 *M*. This concentration has been used throughout. Whenever the concentration of sodium dodecylsulfonate was below 0.03 *M*, enough of the salt was added to the solution just before sampling it to bring the concentration up to this value before addition of the precipitant.

III. RESULTS AND DISCUSSION

1. RELATIVE EFFECTIVENESS OF DIFFERENT ACIDS

The relative effectiveness of various anions has been chiefly determined by measuring the rate at which ammonia is liberated by hydrolysis of amide linkages. This is the rate of a definite chemical reaction involving the breaking of only one bond. The results of many such measurements made with wool are shown in figure 1.

It is obvious that different acids vary enormously in their effectiveness in hydrolyzing the amide bonds of this protein. Thus the rates given by hydrochloric acid and cetylsulfonic acid,[5] differ by a factor of 114. All degrees of effectiveness between these extremes are represented by the other acids studied. Their relative effectiveness as hydrolyzing agents tends to parallel the affinity of their anions for proteins, as previously reported [9].

A number of other acids have been studied which are not included

[5] Because of its low solubility, cetylsulfonic acid was tested at a lower concentration (0.02 *M*), but the total concentration of acid was 0.05 *M*, as in the other experiments.

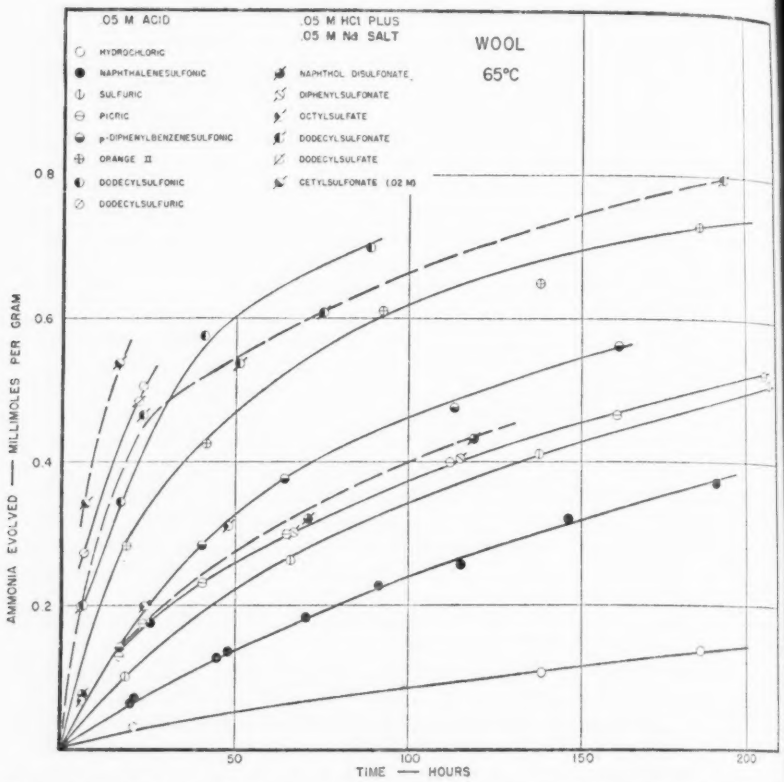


FIGURE 1.—*Relative effectiveness of various strong acids in hydrolyzing the primary amide bonds of wool.*

All the acids are compared at the same concentration of hydrogen ion (0.05 *M*) and at the same temperature (65° C). Points crossed by a shilling mark represent measurements obtained with equimolar mixtures with hydrochloric acid of the sodium salts of the anions indicated.

in figure 1. Among them is the homologous series of sulfate half-esters ($ROSO_3H$), for which comparative data are given in table 1. Here a maximum hydrolytic effect appears to be reached with the 14-carbon acid. This effect is a consequence of the lower hydrogen-ion concentration in solutions of the higher homologues, a result of an increasing tendency to form molecular aggregates as their molecular weight increases [10]. The results obtained with the sulfate half-esters are further complicated by the fact that as their molecular weights increase they are increasingly rapidly hydrolyzed at 65° C to give sulfuric acid and the alcohols.[6] Thus with these acids the rate of the hydrolysis is affected by a simultaneous increase in acidity and decrease in the concentration of effective anions as hydrolysis proceeds. This complication does not affect the data obtained with the sulfonic acids (RSO_3H), which are shown in figure 1.

[6] The half periods for this self-hydrolysis, in the case of the highest members of the series, are less than 24 hours.

TABLE 1.—*Relative effectiveness of various sulfate half-esters in accelerating the acid hydrolysis of wool at 65° C*

All the solutions contained 0.05 *M* HCl plus 0.05 *M* sodium salt of the half-esters

Sulfate half-ester	Amide hydrolysis. Time required to liberate 0.3 millimole ammonia per gram	Peptide hydrolysis. Time required to liberate 1.0 millimole of nonammonia nitrogen per gram
	Hours	*Hours*
n-Octyl-	45.2	100
n-Decyl-	11.4	26
n-Dodecyl-	9.8	17
n-Tetradecyl-	9.3	15
n-Hexadecyl-	10.3	21
n-Octadecyl-	12.2	29

2. DEPENDENCE OF REACTION RATE ON CONCENTRATION OF CATALYTICALLY EFFECTIVE ANIONS

The influence of the more effective anions may be appraised, apart from the simultaneous influence of hydrogen ions, by varying the concentration of the sodium salt of a strongly effective anion, at a fixed concentration of one of the least effective acids, i. e., hydrochloric acid. This procedure is justified because the effect of the presence of sodium and chloride ions is relatively small (cf. data for dodecylsulfonate in figure 1).

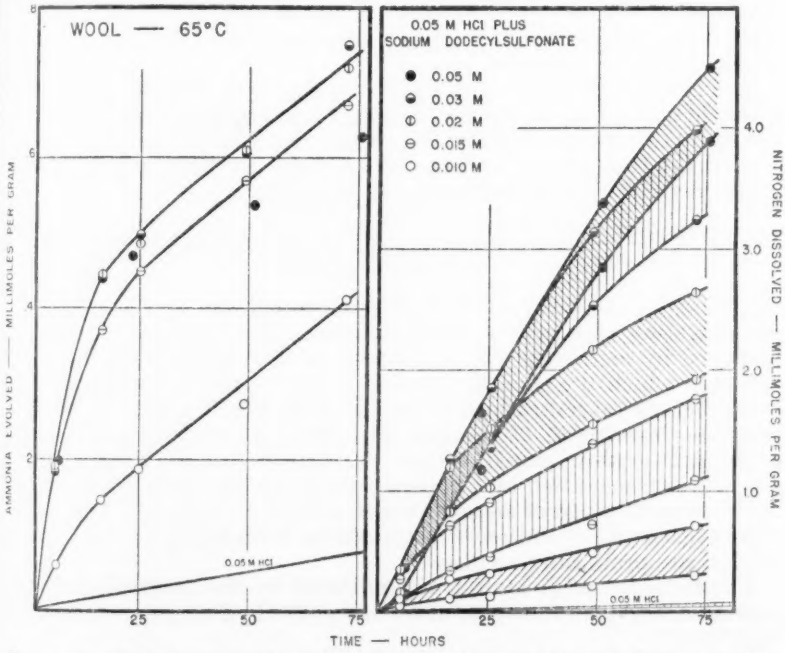


FIGURE 2.—*Hydrolysis of wool in 0.05 M hydrochloric acid at 65° C, as affected by the concentration of dodecylsulfonate ion.*

The hydrolysis of amide bonds is represented in the left-hand frame, and the evolution of dissolved nitrogen, which is a function of the hydrolysis of peptide as well as amide bonds, is represented in the frame on the right. In the latter, experiments with each concentration of anions are represented by a pair of curves, the area between which is shaded. The upper curve of each pair represents the total dissolved nitrogen, and the lower curve represents the nonammonia nitrogen, which refers to the hydrolysis of peptide bonds only.

The results of one such experiment with sodium dodecylsulfonate at 65° C are shown in figure 2. The measurements of amide hydrolysis (left-hand frame) are particularly significant. The rate of hydrolysis increases sharply as the concentration of dodecylsulfonate is increased until a limit is reached at a concentration between 0.015 *M* and 0.02 *M*. Beyond 0.02 *M* no increase in rate occurs.[7] Another limit exists at very low concentrations (<0.008 *M*, not shown in the figure). This limit is practically identical with the curve shown in the figure for hydrochloric acid alone. The lowest concentration at which the rate is appreciably affected by the presence of dodecylsulfonate is stoichiometrically equivalent to the amount of strongly basic groups in the protein.[8] The concentration at which the upper limiting rate is reached corresponds roughly to the sum of the amino groups (0.8 millimole per g) plus the amide groups (0.8 to 0.9 millimole per g) of the wool.

The rate of peptide hydrolysis, as measured by the evolution of nonammonia nitrogen (right-hand frame of fig. 2), is affected by the same range of dodecylsulfonate concentrations in a different way. Low concentrations (0.01 to 0.02 *M*) cause only a small increase in the rate of liberation of nonammonia nitrogen as compared with their effect on the rate of evolution of ammonia. Thus the addition of small amounts of this anion to solutions of hydrochloric acid selectively favors the hydrolysis of amide linkages. With larger amounts the rate of production of nonammonia nitrogen steadily increases (without a corresponding increase in rate of amide hydrolysis). No limit is reached within the range of concentrations studied, and the selective effect disappears.

The rates of liberation of dissolved nitrogen are not proportional in a simple manner to the concentrations of dodecylsulfonate. Instead, the results roughly follow Schütz's rule, which states that the square root of the time required to produce a given enzymatic hydrolysis is proportional to the concentration of enzyme [2].

3. DEPENDENCE OF REACTION RATE ON CONCENTRATION OF HYDROGEN IONS

Although the rate of amide hydrolysis reaches an upper limit as the concentration of effective anions is increased, this limiting rate may be raised by increasing the concentration of hydrogen ions. Experiments in which the concentration of hydrochloric acid was varied at two different concentrations of sodium dodecylsulfonate (fig. 3) show that the dependence of the rate of hydrolysis on hydrogen-ion concentration is also limited. Thus the rate becomes independent of the acid concentration at a concentration five to seven times as high as the concentration of anion at which a limit is reached. The curves representing the evolution of ammonia at both anion concentrations studied are practically identical.

The rate of peptide hydrolysis, indicated by the production of nonammonia dissolved nitrogen, also rises as the hydrogen-ion concentra-

[7] The slight diminution in rate at 0.05 *M* is due to the slightly lower hydrogen-ion concentration of this solution, in which decomposition products more quickly accumulate.

[8] About 0.8 millimole per g, corresponding to about 0.008 *M* at the ratio of wool to solution in these experiments.

tion is increased. Extrapolation of the data appears to indicate that a limiting rate is reached at concentrations of acid somewhat higher than those studied.

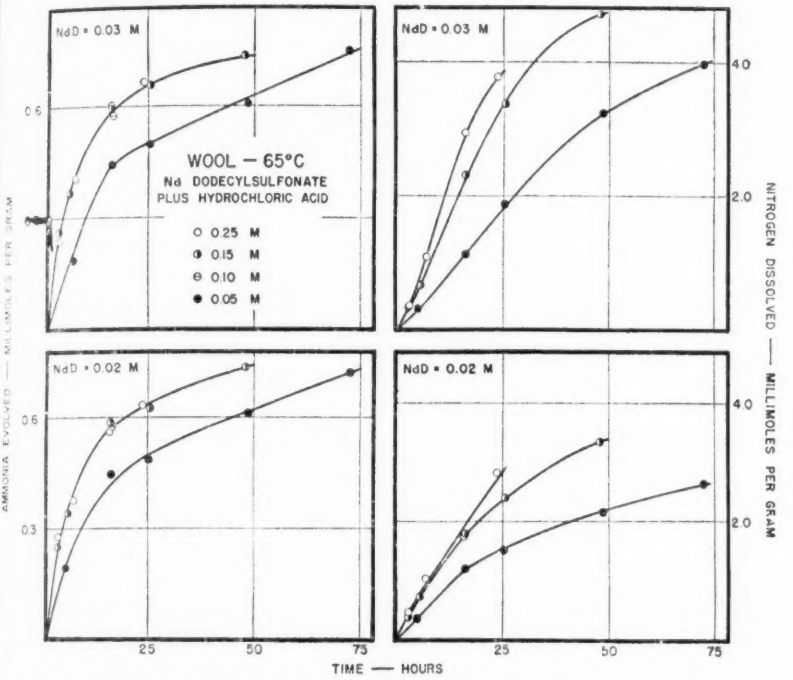


FIGURE 3.—*Relative rates of anion-catalyzed hydrolysis of wool at 65° C, as affected by the concentration of acid.*

Unlike figures 2 and 4, the curves represent the results obtained with different concentrations of acid instead of different concentrations of salt. Results with two different concentrations of dodecylsulfonate are given. Both concentrations are above the level at which the limiting rate of amide hydrolysis in 0.05 *M* acid is attained.

4. DEPENDENCE OF REACTION RATE ON CONCENTRATION OF EFFECTIVE ANIONS AND ON TEMPERATURE AT HIGHER CONCENTRATIONS OF ACID

The course of hydrolysis with respect to time, shown in figures 1 and 2, is affected by changes in pH and in concentration of effective anions, as the products of hydrolysis accumulate. These effects may be reduced by working with higher concentrations of acid. The results of experiments made with three times the concentration of acid represented in figure 2 are shown in figure 4. Data are given for two temperatures.

Owing to the high initial concentration, the change in pH in these experiments never exceeded 0.04 unit. This results in somewhat simpler chemical kinetic relations. The rate of liberation of nonammonia dissolved nitrogen is directly proportional to the concentration of catalytically effective anions, with good approximation. However, the time course of the hydrolysis of amide bonds remains complex. A rapid initial evolution of ammonia (about 0.6 millimole per g) is

followed by a much more gradual reaction, which is hardly faster than when no dodecylsulfonate is present. The course of the reaction in solutions of hydrochloric acid alone appears to be simple; if the amide content of wool is about 0.84 millimole per g,[9] the reaction is of the first order to completion. The reaction catalyzed by dodecylsulfonate follows first-order kinetics only in the period of the initial rapid evolution of ammonia (0.6 millimole per g). Thus it appears that only part of the amide bonds may be susceptible to this catalyst.[10]

The effect of temperature on the rate of hydrolysis is smaller in the presence of the added salt (Q_{10}=2.3) than when acid alone is

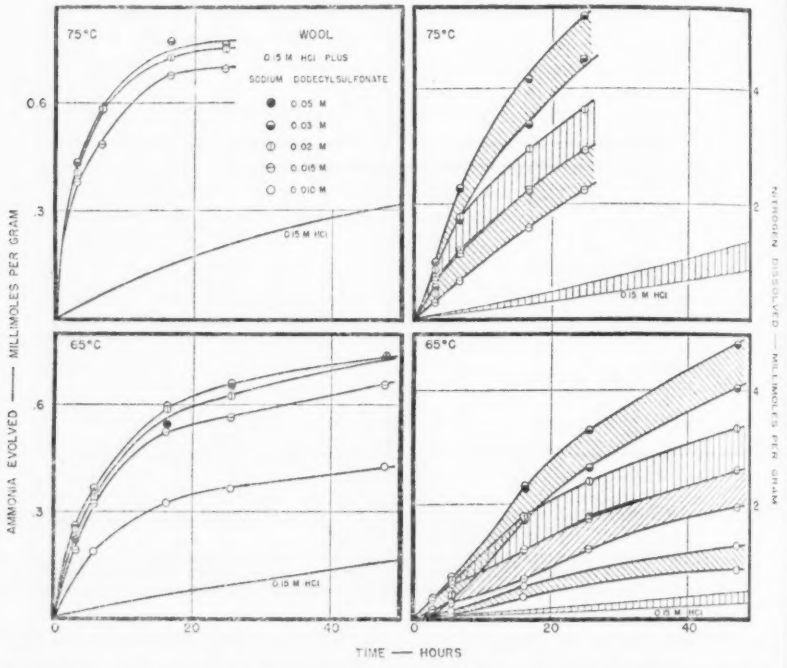


FIGURE 4.—*Hydrolysis of wool in 0.15 M hydrochloric acid, as affected by the concentration of dodecylsulfonate ion and by the temperature.*

used (Q_{10}=3.0). This difference agrees with the common rule that the activation energies of catalyzed reactions are lower than those of the same reactions in the absence of a catalyst. Because of this difference, the catalytic coefficients of the anion (the factor by which it increases the rates) is lower at the higher temperature.

The catalytic coefficient is also lower at 0.15 *M* acid than at 0.05 *M*. Thus, at still higher concentrations, such as those normally used for protein hydrolysis, the catalytic effect of dodecylsulfonate ions may be entirely negligible (cf. section IV).

[9] This value (1.18%) is close to others obtained in this laboratory by a number of different methods.

[10] Of the two amino-acids in wool which may be present in the form of amides, glutamic acid is found in a quantity which corresponds closely with the rapidly evolved portion of the ammonia.

5. RESULTS OBTAINED WITH A SOLUBLE PROTEIN

It is of great interest to determine whether the specific hydrolytic effects of anions which manifest themselves with wool also affect other proteins. Egg albumin has been chosen for investigation as an example of a soluble protein, principally because the careful work of Shore, Wilson, and Stueck [6] provides a close estimate of its amide content.

The results obtained in a series of experiments analogous to those performed with wool (fig. 2) are shown in figure 5. In most important

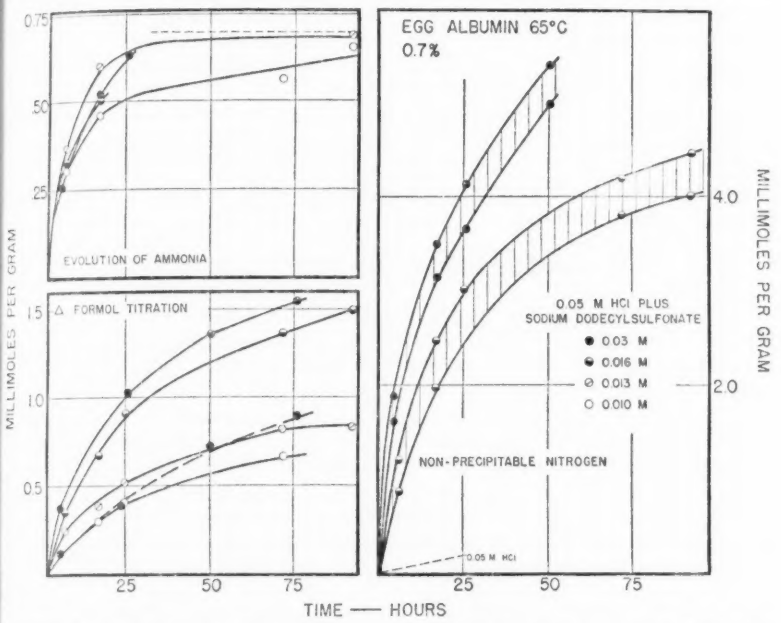


FIGURE 5.—*Hydrolysis of four times crystallized egg albumin in 0.05 M hydrochloric acid at 65° C., as affected by the concentration of dodecylsulfonate ion.*

The horizontal broken line in the upper left-hand frame represents the amide content of egg albumin [6]. The lower left-hand frame represents the change in the formol titer as the result of liberation of carboxyl groups in the protein. The broken line in this frame represents the hydrolysis of peptide bonds at the highest concentration of dodecylsulfonate represented. It was obtained by subtracting the appropriate curve for ammonia evolved from the top curve in this figure.

particulars they are entirely parallel with those obtained with wool. The rate of evolution of ammonia becomes independent of the dodecylsulfonate concentration at a lower concentration (0.011 *M*) than with wool, corresponding to stoichiometric equivalence to the sum of the basic groups plus amide groups of these protein solutions.[11] Unlike wool, egg albumin liberates practically all of its amide nitrogen very quickly; the experimental values thus soon approach those previously reported [6]. Although the state of dispersion of the two proteins is entirely different, the *initial* rate of ammonia evolution is only slightly higher with egg albumin than with wool.

[11] The titration data of Kekwick and Cannan [5] indicate that egg albumin contains per gram about 0.9 millimole of amino and guanidino groups. The amide content [6] is about 0.7 millimole per g. The sum, 1.6 millimoles per g, corresponds to a concentration of about 0.011 *M* at the concentration of protein used in these experiments.

With this soluble protein, the formol titration gives a direct measure of the total number of bonds hydrolyzed. Data obtained by this method, with several concentrations of dodecylsulfonate, are shown in figure 5. The rate of hydrolysis increases without limit within the range of concentrations studied. At the lowest concentration the hydrolysis indicated by the formol titration is hardly larger than that due to breaking amide linkages only, but at higher concentrations the increased rate is obviously due to increased peptide hydrolysis. The selective effect of low concentrations of anions, indirectly indicated by the work with wool, is here directly shown.[12]

The order of effectiveness of the anions tested with wool (table 1 and fig. 1) is the same when egg albumin is the test protein. Although the most effective of the acids tested (cetylsulfonic) has a catalytic coefficient (with respect to hydrochloric acid) of about 200, none of these catalysts approaches closely to the catalytic activity of the proteolytic enzymes, which are substances of much higher molecular weight. Weight for weight, crystalline pepsin at 35.5° is about 3,000 times more effective than cetylsulfonate at 65° in liberating carboxyl groups in egg albumin.

IV. MECHANISM OF THE CATALYSIS

The existence of an upper limit to the anion-catalyzed rate of hydrolysis of amide bonds, and the absence of a similar limit to the rate of hydrolysis of the more numerous peptide bonds, within the range of anion concentrations studied, suggest a mechanism of hydrolysis which involves combination of the effective anions with the groups hydrolized. This suggestion is supported by the stoichiometric correspondence between the amounts of dodecylsulfonate which suffice to give the maximum rate and the number of strongly basic plus amide groups in the proteins tested, which indicates that small amounts of anions combine preferentially with the amide groups.

The stoichiometric interpretation of this limit has been supported by showing that, under a given set of conditions, the *amount* of dodecylsulfonate present, relative to the amount of wool, rather than its *concentration* in solution, determines the hydrolytic rate. One of the solutions represented in figure 2 (0.02 *M* in sodium dodecylsulfonate and 0.05 *M* in hydrochloric acid) was diluted with an equal volume of 0.05 *M* hydrochloric acid. The *concentration* of effective anion thus fell below that required for the attainment of the maximum rate of amide hydrolysis in the earlier experiments, although the total amount remained unchanged. The rate of production of ammonia remained as high as if the dodecylsulfonate had not been diluted.

The result of the experiment just described depends on the fact that dodecylsulfonate ion is almost quantitatively transferred from the solution to the fibers [9]. With anions having a lower affinity for wool, the concentration at which a limiting rate is attained should be higher than with dodecylsulfonate, and should not be assigned stoichiometric significance. Data obtained with an anion of only moderate affinity for wool, octylsulfate, are shown in figure 6.

[12] The formol data also indicate that only about 10 percent of the peptide bonds in the protein were hydrolyzed when two-thirds of the protein was not precipitated with trichloroacetic acid.

The concentration of octylsulfate at which a maximum rate of amide hydrolysis is attained is at least five times as great as in the experiments with the ion of higher affinity. However, the maximum rate obtained with octylsulfate is only slightly lower than the maximum attained with dodecylsulfonate. Thus, the two anions, when *combined with the protein*, are almost equally effective.[13]

Since the maximum anion-catalyzed rates attained at a given acid concentration may be increased by raising the concentration of acid, it is apparent that hydrogen ions, as well as anions, participate in the

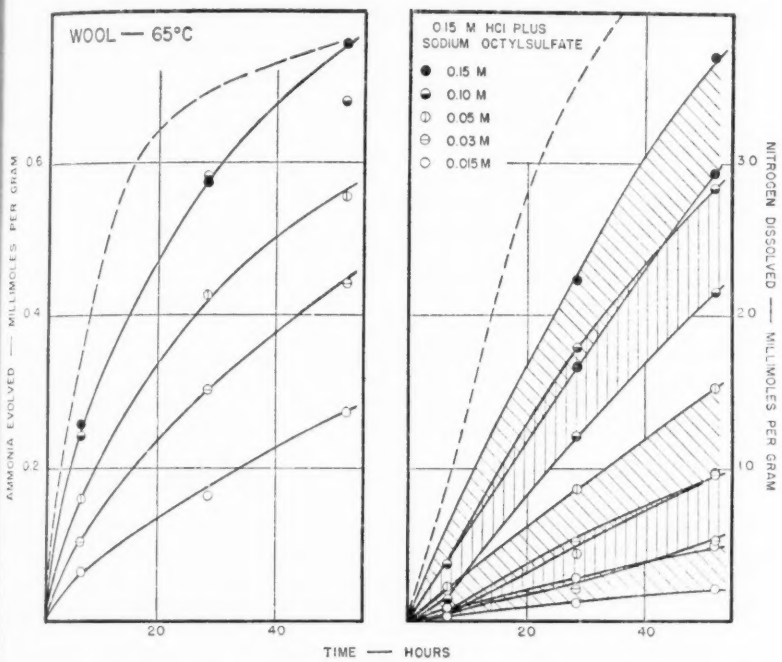


FIGURE 6.—*Hydrolysis of wool at 65°C, as affected by the concentration of octylsulfate ion.*

The concentration of acid (0.15 *M*) is higher than in the experiments represented in figure 2. The broken lines, included for comparison, represent data obtained with the same concentration of acid, and 0.03 *M* sodium dodecylsulfonate, a concentration well in excess of the amount required to attain the maximum rate of amide hydrolysis with this anion.

reaction. However, the fact that the effect of varying the concentration of acid is also limited to relatively low concentrations (<0.1 *M*) shows that its influence is not a common case of simple hydrogen-ion catalysis. In the latter, only an exceedingly small fraction of the hydrogen ions combine with the substrate molecules. In the present case, a very considerable part must combine since saturation of the combining groups in the protein is evidently attained at relatively low concentrations. Under ordinary conditions, amide and peptide groups are too weakly basic to combine to any appreciable extent with hydrogen ions at these concentrations of acid, but their

[13] The small residual differences between the limiting effects of various anions may be attributed to a kinetic salt effect of the uncombined ions.

readiness to combine with hydrogen ions may be greatly increased by acquiring a negative charge by combination with an anion. Similar effects of charge on the strengths of acids and bases have been discussed by the present authors [8, 9] and have been treated theoretically by many others.

The fact that much more hydrogen ion than dodecylsulfonate ion must be present to attain the maximum rate of amide hydrolysis indicates that the proteins combine with hydrogen ion less readily than with dodecylsulfonate. This indication is consistent with the relative affinities for wool of these two ions, as previously reported [9]. If insufficient hydrogen ion is present, the amide groups may be fully combined with anions of high affinity without attaining the maximum rate of hydrolysis (fig. 3). This maximum is attained with full combination with hydrogen ions.

Accordingly, the influence of the catalytically active anions on both amide and peptide groups is primarily exerted by promoting the combination of hydrogen ions with these weakly basic groups in dilute acid solutions. The agent which actively induces the liability of the C-N bonds is the combined hydrogen ion.[14] In a sufficiently acid environment the catalytic influence of the anions should disappear (cf. p. 322). Unlike the general basic catalysis defined by Brønsted, the catalytic activity of the anion depends on its affinity for protein rather than on its inherent strength as a base.

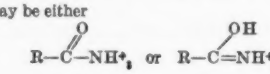
Whether the mechanism described is applicable to other amides, and whether the action of anions of high molecular weight gives a clue to the still more effective action of proteolytic enzymes, cannot be determined without further work.

V. POTENTIAL FIELDS OF APPLICATION

The practical consequences of these phenomena arise partly from the possibility they afford of hydrolyzing proteins under milder conditions than those which are habitually employed, both with respect to concentration of acid and to temperature. The selective action of low concentrations of the catalysts in hydrolyzing amide bonds also may be useful in analysis, or in the production of modified proteins. This selective effect is favored by (a) use of anion concentrations only slightly greater than are required for combination with the amino and guanidino groups of the protein, (b) low acidities, such as 0.05 *M*, (c) relatively low temperatures, such as 65° C. The result is also influenced by the choice of anion, a higher selective action resulting from the use of cetylsulfonate or diphenylbenzenesulfonate than from the use of any other ions tested.

Mild methods of protein hydrolysis are of value in the preparation of hydrolysates for intravenous or oral use in medicine [3], because they are less likely to impair the nutritive value of the digested material. Likewise, it is sometimes desirable to dissolve or destroy protein materials without affecting other materials which may be associated with them. The removal of glues and albuminous coatings from cellulosic materials is one instance; the purification of enzymes and other biological products is another.

[14] The reactive intermediate may be either



VI. REFERENCES

[1] M. L. Anson, J. Gen. Physiol. **23,** 239 (1939).
[2] S. Arrhenius, Quantitative Laws in Biological Chemistry (Harcourt-Brace, Inc., New York, 1915.)
[3] R. Elman, Proc. Soc. Exp. Biol. & Med. **36,** 867 (1937); **43,** 14 (1940); A. White and R. Elman, J. Biol. Chem. **143,** 797 (1942).
[4] J. H. Northrop, J. Gen. Physiol. **16,** 41 (1932).
[5] R. A. Kekwick, and R. K. Cannan, Biochem. J. **30,** 227 (1936).
[6] A. Shore, H. Wilson, and G. Stueck, J. Biol. Chem. **112,** 407 (1935).
[7] J. Steinhardt, J. Biol. Chem. **141,** 995 (1941); Federation Proc. **1,** 136 (1942).
[8] J. Steinhardt, C. H. Fugitt, and M. Harris, J. Research NBS **26,** 293 (1941) RP1377; Am. Dyestuff Rptr. **30,** 223 (1941); Textile Research **11,** 259 (1941).
[9] J. Steinhardt, C. H. Fugitt, and M. Harris, J. Research NBS **28,** 201 (1942) RP1453; Am. Dyestuff Rptr. **31,** 77 (1942).
[10] P. van Rysselberghe, J. Phys. Chem. **43,** 1049 (1939).

Washington, September 7, 1942.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1504

Part of Journal of Research of the National Bureau of Standards, Volume 29, November 1942

FRESNEL REFLECTION OF DIFFUSELY INCIDENT LIGHT

By Deane B. Judd

ABSTRACT

The reflection factor of a plane boundary between two media has been computed by the Fresnel formula for unpolarized, perfectly diffused incident light as a function of the relative index of refraction of the media. Because of total internal reflection, the factors depend importantly upon whether the diffuse flux is incident externally or internally. For example, diffuse light in air incident on the plane surface of glass of index 1.5 is 9.2 percent reflected; but if the perfectly diffuse light is incident internally, the reflection factor is 60 percent.

In the optical specification of light-scattering materials[1] by means of the absorption and scattering coefficients of the Kubelka-Munk theory,[2] it is frequently necessary to consider the effect of both external and internal reflection of light diffusely incident on a plane boundary between two media of different indices of refraction.[3] The reflectance at such a boundary has therefore been computed by application of the well-known Fresnel formula. The results are shown in table 1 as a function of the ratio, m, of the index of refraction of the denser medium to that of the rarer. The reflectance for perpendicular incidence, r, computed from the formula

$$r=(m-1)^2/(m+1)^2 \tag{1}$$

is also shown in the table.

The reflectance for completely diffused unpolarized light incident externally was computed from the approximate formula given by McNicholas:[4]

$$r=\sum_0^{\pi/2} r_\phi \sin 2\phi\Delta\phi/\sum_0^{\pi/2} \sin 2\phi\Delta\phi, \tag{2}$$

where r_ϕ is the reflectance by the Fresnel formula for unpolarized light incident on the surface from the rarer medium at an angle, ϕ, from the perpendicular to the surface. The angular interval, $\Delta\phi$, used in these summations was 0.04 radian.

[1] Deane B. Judd (with the collaboration of W. N. Harrison, B. J. Sweo, E. F. Hickson, A. J. Eickhoff, Merle B. Shaw, and George C. Paffenberger), *Optical specification of light-scattering materials*, J. Research NBS **19**, 287 (1937) RP1026.

[2] P. Kubelka and F. Munk, *Ein Beitrag zur Optik der Farbanstriche*, Z. tech. Physik **12**, 593 (1931).

[3] J. W. Ryde and B. S. Cooper, *Scattering of light by turbid media, I*, Proc. Roy. Soc. (London) [A] **131**, 451 (1931).
B. W. King, Jr., *Effect of particle size and index of refraction on reflectance*, J. Ceramic Soc. **23**, 221 (1940).
J. S. Preston, *The properties of diffusing glasses with special reference to surface effects*, Proc. Intern. Illumination Cong. **1**, 373; 1931 (London, 1932).

[4] H. J. McNicholas, *Absolute methods in reflectometry*, BS J. Research **1**, 29 (1928) RP3. See equation 18, p. 50.

TABLE 1.—*Reflectance of unpolarized light at a plane boundary between two media as a function of their relative index of refraction, m*

m	Reflectance for perpendicular incidence	Reflectance for completely diffuse incidence		m	Reflectance for perpendicular incidence	Reflectance for completely diffuse incidence	
		External reflection	Internal reflection			External reflection	Internal reflection
1.00	0.00000	0.0000	0.000	1.31	0.01801	0.0628	0.454
1.01	.00002	.0028	.022	1.32	.01902	.0644	.463
1.02	.00010	.0055	.044	1.33	.02006	.0660	.472
1.03	.00022	.0082	.064	1.34	.02111	.0676	.480
1.04	.00038	.0108	.084	1.35	.02218	.0692	.489
1.05	.00059	.0134	.103	1.36	.02327	.0707	.497
1.06	.00085	.0158	.122	1.37	.02437	.0723	.505
1.07	.00114	.0183	.140	1.38	.02549	.0738	.513
1.08	.00148	.0206	.158	1.39	.02663	.0754	.520
1.09	.00185	.0230	.175	1.40	.02778	.0769	.528
1.10	.00227	.0252	.192	1.41	.02894	.0784	.536
1.11	.00272	.0274	.208	1.42	.03012	.0800	.543
1.12	.00320	.0294	.224	1.43	.03131	.0815	.550
1.13	.00372	.0314	.240	1.44	.03252	.0830	.557
1.14	.00428	.0334	.254	1.45	.03373	.0845	.564
1.15	.00487	.0353	.269	1.46	.03497	.0860	.571
1.16	.00549	.0371	.283	1.47	.03621	.0875	.577
1.17	.00614	.0389	.296	1.48	.03746	.0890	.584
1.18	.00682	.0407	.309	1.49	.03873	.0904	.590
1.19	.00753	.0425	.322	1.50	.04000	.0919	.596
1.20	.00826	.0443	.335	1.51	.04129	.0934	.602
1.21	.00903	.0461	.347	1.52	.04258	.0948	.608
1.22	.00982	.0478	.359	1.53	.04389	.0963	.614
1.23	.01064	.0496	.371	1.54	.04520	.0977	.619
1.24	.01148	.0513	.382	1.55	.04652	.0992	.624
1.25	.01235	.0530	.393	1.56	.04785	.1006	.630
1.26	.01323	.0546	.404	1.57	.04919	.1020	.635
1.27	.01415	.0563	.414	1.58	.05054	.1035	.640
1.28	.01508	.0579	.424	1.59	.05189	.1049	.645
1.29	.01604	.0596	.434	1.60	.05325	.1063	.650
1.30	.01701	.0612	.444				

The reflectance for completely diffused unpolarized light incident internally was computed from the similar formula:

$$r=\sum_{0}^{\pi/2} r_\theta \sin 2\theta\Delta\theta / \sum_{0}^{\pi/2} \sin 2\theta\Delta\theta, \tag{3}$$

where r_θ is the reflectance by the Fresnel formula for unpolarized light incident on the surface from the denser medium at an angle, θ, from the perpendicular to the surface. The angular interval, $\Delta\theta$, used in these summations was 0.04 radian except for the interval of 0.04 radian containing the critical angle ($\theta_c=\sin^{-1} 1/m$) for which it was taken as 0.0005 radian.

Values of r_ϕ were read directly from tables published by Moon.[5] Values of r_θ for θ less than the critical angle were found by reading the value of r_ϕ from Moon's table for ϕ equal to the angle whose sin is $m \sin \theta$. For θ greater than the critical angle, r_θ is, of course, equal to 1.

The summations were carried out for $m=1.1$, 1.2, 1.3, 1.4, 1.5, and 1.6. Intermediate values were found by third-difference osculatory interpolation [6] with the terminal intervals filled in by extrapolation of the third-differences. The uncertainty is estimated to be less than 2 in the last figure given. The values of reflectance for external

[5] Parry Moon, *A table of Fresnel reflection*, J. Math. Phys. **19**, 1 (1940).

[6] J. W. Glover, *Derivation of the United States Mortality Table by osculatory interpolation*, Quart. Pub. Am. Statistical Assoc. **12**, 90 (1910).

D. B. Judd, *Extension of the standard visibility function to intervals of 1 millimicron by third-difference osculatory interpolation*, BS J. Research **6**, 465 (1931) RP289.

diffuse incidence agree well with those computed by Ryde and Cooper (see footnote 3) from a formula derived by Walsh.[7]

Figure 1 shows as a function of m, reflectance for perpendicular incidence, reflectance for external diffuse incidence, and reflectance for internal diffuse incidence. It may be seen that there is consider-

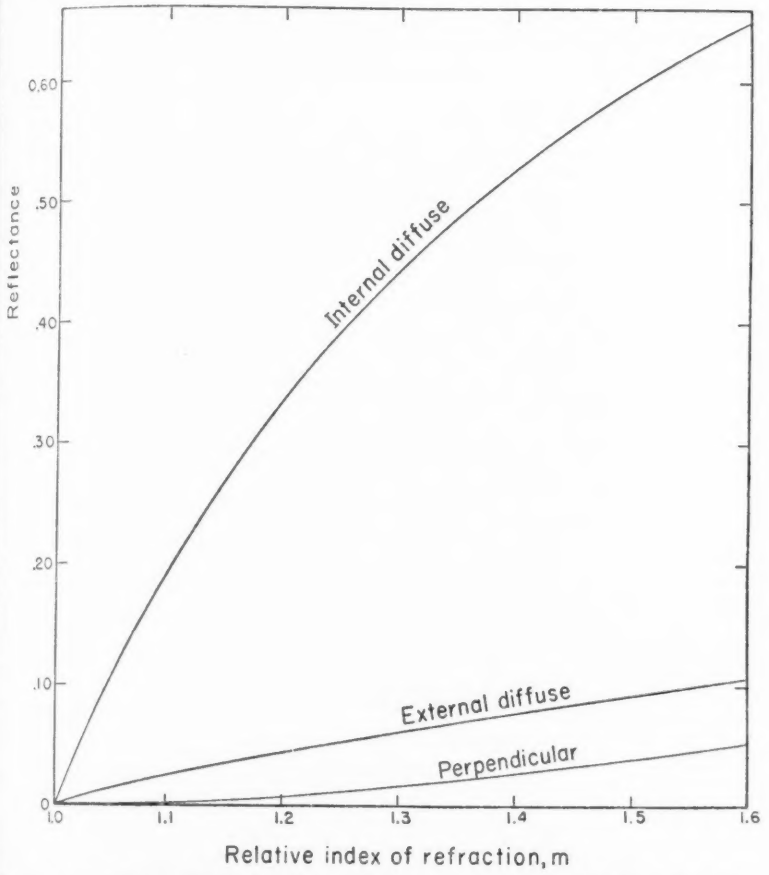


FIGURE 1.—*Fraction of incident light reflected from a plane interface for three angular conditions of illumination: (a) perpendicular incidence, (b) perfectly diffuse incidence from the less dense medium (external), and (c) perfectly diffuse incidence from the denser medium (internal).*

Note that internal reflection of diffusely incident light takes place to a considerable degree even at boundaries between media of only slightly differing index of refraction (m approaching 1.0).

able difference between these functions not only in amount but also in the shapes of the curves which represent them.

Preston,[3] Ryde,[3] and Duntley [8] have correctly warned that internal reflectance is sharply dependent on the degree of approach to complete diffusion of the incident light. For the same reasons it is

[7] J. W. T. Walsh, *The reflection factor of a polished glass surface for diffused light*, Dept. Sci. Ind. Res. (Brit.), Illumination Research Tech. Pap. **2**, 10 (1926).
[8] S. Q. Duntley, *The optical properties of diffusing materials*, J. Opt. Soc. Am. **32**, 61 (1942).

also sharply dependent upon the degree of approach of the surface to a perfect plane. A slightly wavy or scratched surface bounding a diffusing medium, or a surface exhibiting an "orange-peel" texture should be expected to have values of internal reflectance considerably lower than those for a perfect plane.

Acknowledgment is made to Margaret M. Balcom for carrying out the computations.

WASHINGTON, August 1942.

U. S. Department of Commerce — National Bureau of Standards

RESEARCH PAPER RP1505

Part of Journal of Research of the National Bureau of Standards, Volume 29, November 1942

WEAR TESTING OF CARPETS

By Herbert F. Schiefer

ABSTRACT

The NBS and Shawmut machines for testing the wear resistance of carpets, a gage for measuring the thickness of carpets, and an instrument for measuring the length of a tuft of pile from a carpet are described. The effects of the height of the vacuum-cleaner nozzle above the pile, the amount of suction at the nozzle, and the relative humidity and temperature of the air in which the test is made, on the results obtained with the NBS machine were studied. The effect of systematic changes in carpet construction on the wear resistance was investigated with each machine and under severe service conditions. Tests on 24 carpets of Axminster, velvet, and Wilton weaves were made on the two types of machines in several laboratories, and the results obtained in the different laboratories were correlated with each other and also with the results of 3 years of service tests on the same carpets. The correlations were highly significant, but large systematic differences between the weaves and between the laboratories were obtained. The latter difference is attributed primarily to a lack of uniformity in the testing procedures. Three types of vacuum-cleaning systems were used during the service tests, and their effect on the wear of the carpets and the effectiveness of cleaning were observed. The *S* index, which is the time required to wear the pile of a carpet down to one-fourth of the matted pile thickness, corresponds closely with the time at which a carpet in a service test would be discarded on account of visible wear. The deviation of the *S* index of a single test from the average is less than 10 percent in 9 trials out of 10. The nature of the wear produced by the two machines on the pile fibers was found to be similar to that produced during the service tests. The analyses of carpets do not yield sufficient data to determine the probable durability of carpets in general. The relative wear of carpets for a given use can be evaluated by means of laboratory wear tests. For general interlaboratory comparison of the relative wear resistance of carpets, the testing machines and the testing procedures must be rigidly standardized and controlled.

CONTENTS

	Page
I. Introduction	334
II. Testing machines	334
1. NBS machine for testing the wear of carpets	334
2. Shawmut machine for testing the wear of carpets	337
3. Thickness gage for carpets	338
4. Instrument for measuring the length of a tuft of pile	339
III. Testing procedures	340
1. Analysis of carpet construction	340
2. Thickness	340
3. Wear of carpets	340
(a) NBS machine	340
(b) Shawmut machine	341
(c) Service tests	341
4. Wear indices	341
IV. Materials tested	343
V. Standardization of test on NBS machine	348
1. Effect of braking torque, downward force at each pulley, and speed of turntable	348
2. Effect of relative humidity and temperature	348
3. Effect of height of nozzle and suction at the nozzle	349

487101—42——3

Page
VI. Results 349
1. Wear indices 349
2. Service tests 351
3. Comparison of service, NBS, and Shawmut tests on 24 carpets 357
4. Comparison of wear tests with analyses of carpets 359
5. Interlaboratory tests 362
6. Effect of type of vacuum-cleaning system on the service wear of carpets 367
7. Nature of wear of the fibers 370
8. Correlation of wear test results with analysis of carpets 370
9. Limitations of wear-testing machines 376
VII. Summary 377

I. INTRODUCTION

After the publication of Research Papers RP315 and RP640,[1] describing the NBS machine for testing the wear of carpets and discussing the results obtained with it, extensive wear-testing of carpets was undertaken in the laboratories of the carpet industry. Section IV on Pile Floor Coverings, of Subcommittee A–3, Committee D–13, American Society for Testing Materials, served as a clearing house for the discussion of these tests. It became apparent from these tests that there were some inconsistencies in the results obtained, between different laboratories and also within the same laboratory, on carpets of similar quality. It was found that the inconsistencies in the results could be attributed in a large measure to a lack of uniformity of production in carpet manufacturing. This information led to the early use of statistical control by a number of carpet manufacturers, following the method introduced by Shewhart.[2] The results of the tests indicated also that some of the inconsistencies resulted from a lack of standardization of the wear-testing equipment, testing conditions, testing procedure, and method of evaluation of the results.

The investigation which forms the basis of this paper was undertaken in cooperation with Subcommittee A–3 to obtain information on the influence of a number of testing factors on the results and to shed much needed light on the interpretation of the results obtained in testing carpets for wear. The improved NBS machine and the Shawmut machine for testing the wear resistance of carpets, a gage for measuring the thickness of carpets, and an instrument for measuring the length of a tuft of pile from a carpet are described. The results of laboratory tests of the wear of 24 carpets are compared with those obtained on the same carpets when subjected to 3 years of severe wear in actual service. Additional information is presented on the relationship between construction factors of carpets and the resistance to wear.

II. TESTING MACHINES

1. NBS MACHINE FOR TESTING THE WEAR OF CARPETS

The NBS machine for testing the wear of carpets is shown in figure 1. The specimen, circular in shape, is fastened to a metal turntable, 17 in. in diameter, shown in figures 2 and 3. The turntable is placed

[1] H. F. Schiefer and A. S. Best, Carpet wear testing machine, BS J. Research **6**, 927–936 (1931) RP315. Herbert F. Schiefer and Richard S. Celveland, Wear of carpets, BS J. Research **12**, 155–166 (1934) RP640.

[2] W. A. Shewhart, Economic Control of Quality of Manufactured Product (D. Van Nostrand Co., Inc., New York, N. Y., 1931).

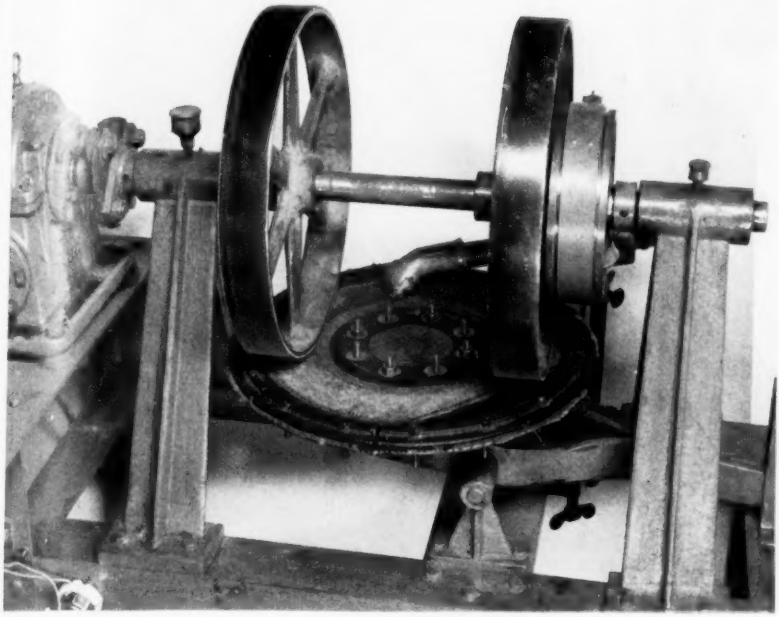


FIGURE 1.—*The NBS machine for testing the wear of carpets.*

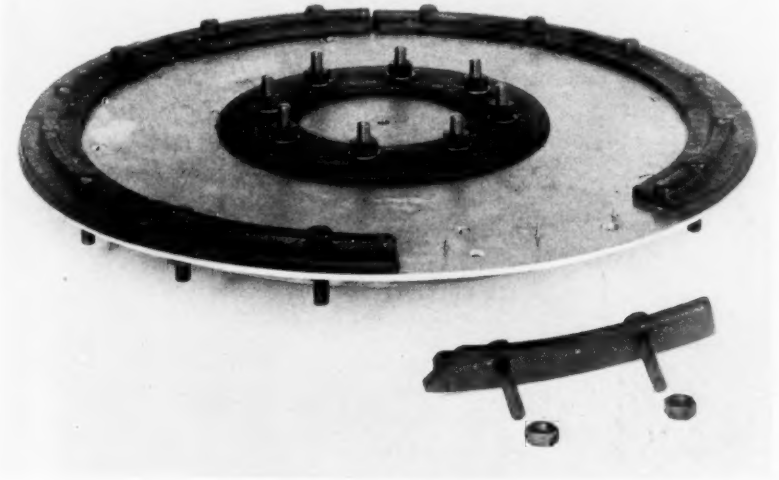


FIGURE 2.—*Metal turntable.*

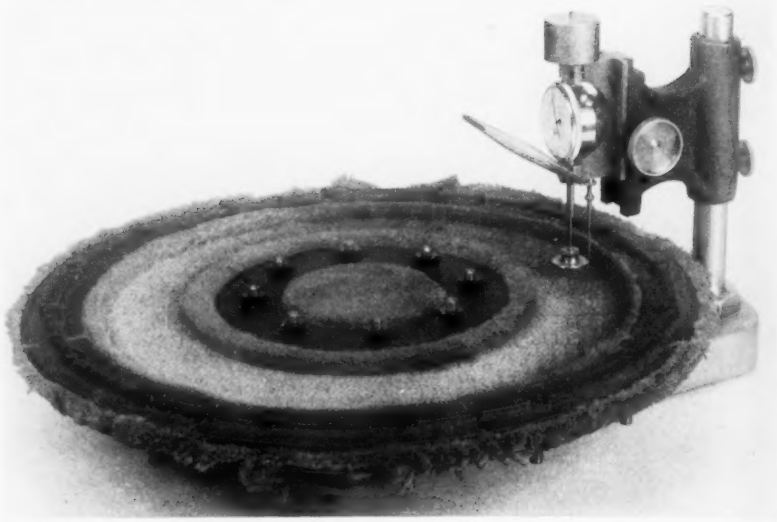


FIGURE 3.—*Gage for measuring thickness of carpet mounted on turntable.*

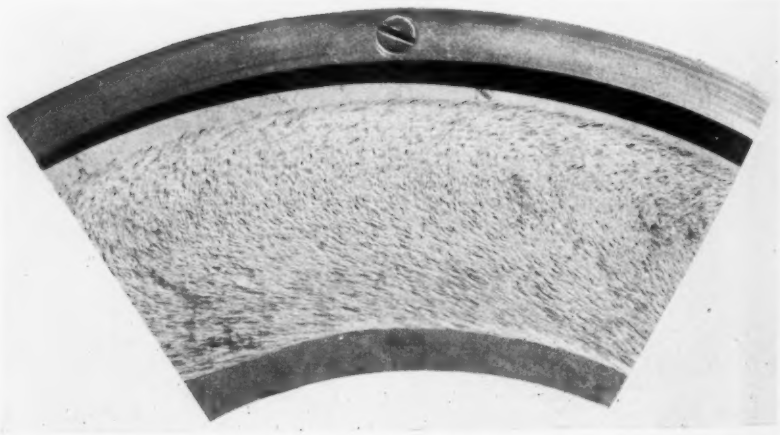


FIGURE 4.—*Specimen of tile showing the twisting action produced by the NBS carpet-wear-testing machine.*

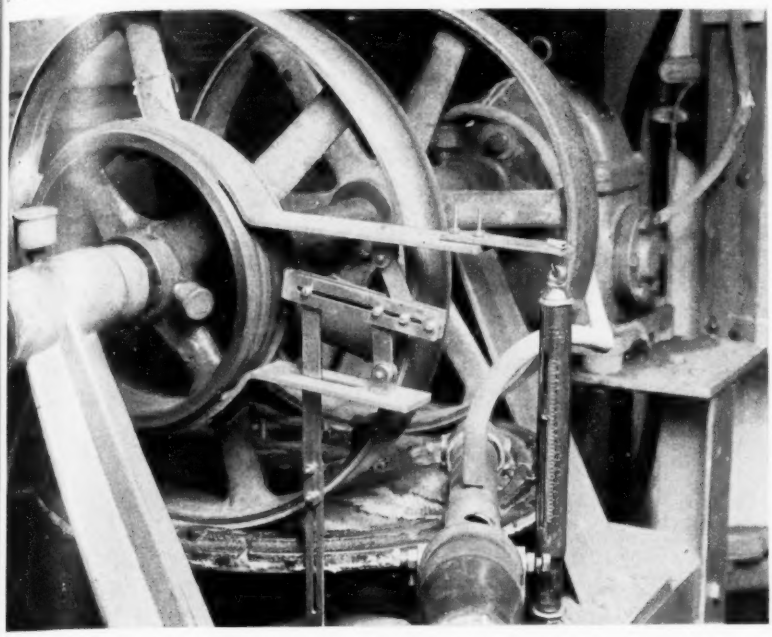


FIGURE 5.—*Link-type brake for the NBS carpet-wear-testing machine.*

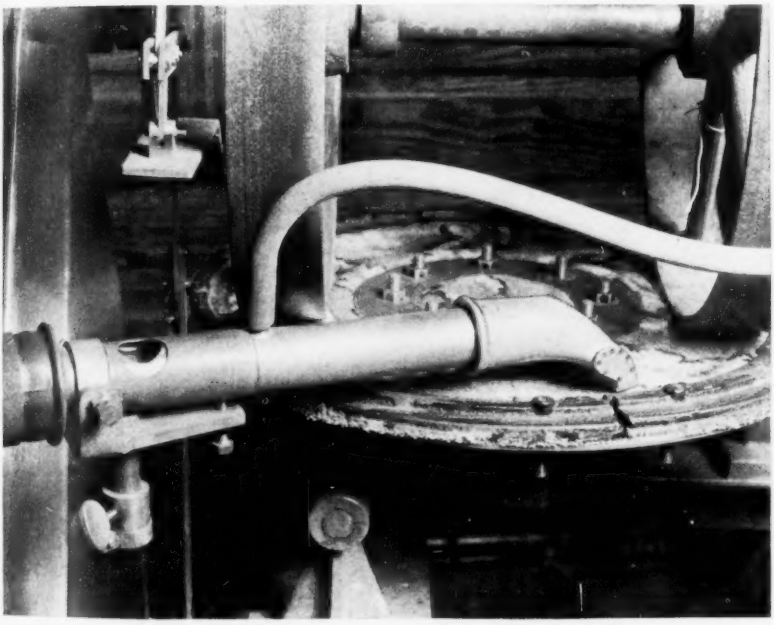


FIGURE 6.—*Nozzle assembly of vacuum cleaner.*

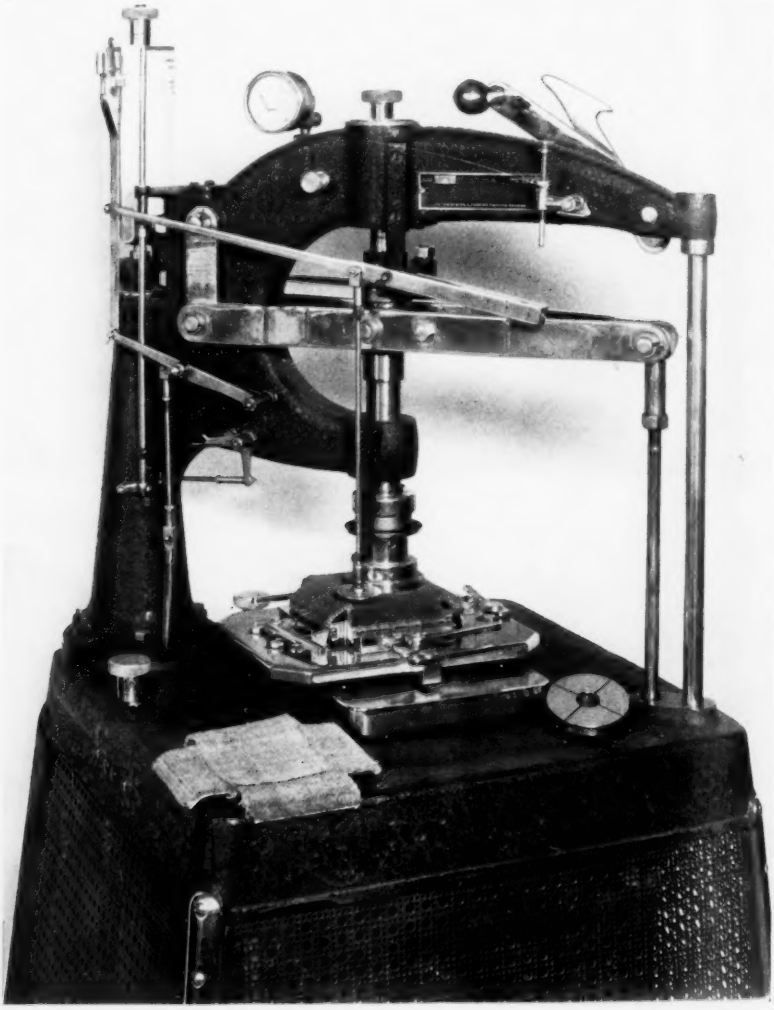


FIGURE 7.—*Shawmut machine for testing the wear of carpet.*

over the end of a vertical shaft which is mounted in a special bearing at one end of a lever, so that when a weight is hung at the other end of the lever the carpet is brought to bear with the same vertical force against each of two leather-covered pulleys. The metal segments that are bolted to the turntable and the pointed pins which pierce the backing of the carpet specimen are effective in holding the specimen firmly during a test. The specimen is mounted with sufficient initial tension so that the exposed surface is flat and free from wrinkles. It is convenient to use a template, which exactly matches the turntable surface, in preparing the specimens for this test. The turntable is readily removed from the machine and may be transferred to a special gage (fig. 3) for measuring the thickness of the carpet specimen.

One of the pulleys which bears against the specimen during a test is driven by a shaft connected through a reduction gear to a motor. This pulley drives the turntable by friction. The other pulley, which is free to rotate on the driving shaft, is used as a brake to produce slipping of both pulleys on the carpet specimen as it rotates. A slight twisting action is produced on the pile of the carpet, because the carpet specimen is rotated in a plane perpendicular to the plane of rotation of the pulleys. This twisting action is shown qualitatively in figure 4 on a specimen of tile for floors. This specimen was tested with the driving pulley and using a coarse abrasive in place of the leather. The markings on the surface of the specimen indicate the twisting action.

The load on the brake is indicated by the spring balance shown in figure 5. This load may be varied slightly by means of a wing nut at the bottom of the spring balance. The link-type brake [3] shown in figure 5 has been found satisfactory for maintaining constant the load on the brake during a test. Large variations in the load on the brake can be obtained by changing the relative positions of the links. A Prony brake is also satisfactory, but requires manual adjustment and closer watching during operation.

The nozzle used in conjunction with a vacuum system to remove the worn material from the specimen during a test is shown in figure 6. The nozzle opening is 2 by ¼ in. A connection to a manometer, located 9 in. from the opening of the nozzle, is provided to indicate the amount of suction. It was possible to maintain a suction of 12 cm Hg with the vacuum system when the opening of the nozzle was closed. The amount of suction can be varied by rotating the sleeve surrounding the nozzle tube. This rotation varies the amount of air which enters the nozzle tube through an opening of the sleeve. The mounting of the nozzle tube permits rotations about vertical and horizontal axes. The entire nozzle assembly can be displaced in a vertical direction. The rotation about the horizontal axis is controlled by a screw. The distance between the nozzle and the specimen can thus be easily adjusted and maintained at a constant value. This distance is measured by means of a plate, having the selected thickness, which can just be inserted between the pile and the bottom of the nozzle.

The distance between the centers of the two leather-covered pulleys is 11 in. The width of each pulley is 2 in. and the diameter 15 in. The leather is vegetable-tanned belting leather, curried to contain 10 ±2 percent of extractable oil. Each strip is 2¼ in. wide, at least 48 in. long without any splices, and is cut from the butt center between 8

[3] This link-type brake was designed by John Langton in the laboratory of Alex. Smith & Sons Carpet Co., Yonkers, N. Y.

and 12 in. from the backbone. The flesh side is leveled by machine, so that the average thickness of the piece is 0.205 ±0.005 in. An endless belt is made of each strip to fit very snugly on the pulley. The leather is fastened to the pulley with fish glue. The glue is applied to the flesh side of the leather and to the pulley surface, which should be rough. The pulley surface should be clean, dry, and hot when the glue is applied. This can be accomplished by immersing the pulley in boiling water for 15 minutes just prior to mounting the leather. After the glue is dry, the pulley is mounted in a lathe and the leather is turned down to a width of 2 in. and an over-all diameter of pulley and leather of 15$\frac{5}{16}$ in. The surface is then polished with fine sandpaper. The machine should be operated for at least 100,000 revolutions of the turntable, using any available carpet specimen that will not wear out during this period, to produce a highly polished surface on the leather. This highly polished surface is retained for several million revolutions of the turntable during normal testing.

The speed of the driving shaft is constant in the NBS testing machine, and depends upon the speed of the motor and the ratio of the reduction gear. The speeds of the turntable and braking pulley depend upon the speed of the driving pulley, the frictional forces between the leather and the carpet specimen, and upon the braking torque. The speed of the driving pulley and the braking torque can be maintained constant. The frictional force between the carpet specimen and the pulleys may vary, however, with different carpets and during a test of the same specimen. The relationship between the speeds of the pulleys and the turntable, for a considerable range of speeds of the driving pulley, is such that the amount of slippage at the center of the driving pulley relative to the carpet specimen remains very nearly equal to the amount of slippage at the center of the braking pulley relative to the carpet specimen. The slippages at the centers of the two pulleys relative to the carpet specimen are in opposite directions and range between 9 and 13 percent during normal testing.

In a series of tests for which the braking torque was 7.5 lb ft and the speed of the driving pulley 64 rpm, the speed of the turntable and of the braking pulley had the frequency distributions given in table 1. It was also found that the speeds of the two pulleys and of the turntable are related linearly to each other over a 20-percent change in speed of the driving pulley. In other words, for a given increase in speed of the turntable, the percentage increase in the speed of the driving pulley is equal to the percentage increase in speed of the braking pulley. If the speed of the driving pulley and the braking torque are maintained constant during a test, it is possible that the frictional force between the carpet and the leather of the pulleys may change owing to a change in the fibers of the pile of the specimen and in the surface of the leather. If the frictional force is increased, then the speeds of the turntable and of the braking pulley are automatically increased and the amount of slippage between the pulleys and the pile of the carpet specimen is decreased. The energy expended on the specimen per revolution of the turntable probably remains very nearly constant for these conditions. This constant expenditure of energy per revolution of the turntable probably explains why no marked increase in temperature of the leather and of the pile of the specimen has been observed in any of the carpets tested on this type of machine.

TABLE 1.—*Frequency distribution of the speeds of the turntable and braking pulley when the speed of the driving pulley and the braking torque were maintained at 64 rpm and 7.5 pound-feet, respectively*

Turntable		Braking pulley	
Speed	Frequency	Speed	Frequency
rpm		*rpm*	
78	1	47	1
79	10	48	0
80	25	49	1
81	16	50	11
82	6	51	29
83	1	52	15
		53	2

2. SHAWMUT MACHINE FOR TESTING THE WEAR OF CARPETS

The Shawmut machine for testing the wear of carpets is shown in figure 7. The test specimen is 6½ in. square. A square 1½ inches

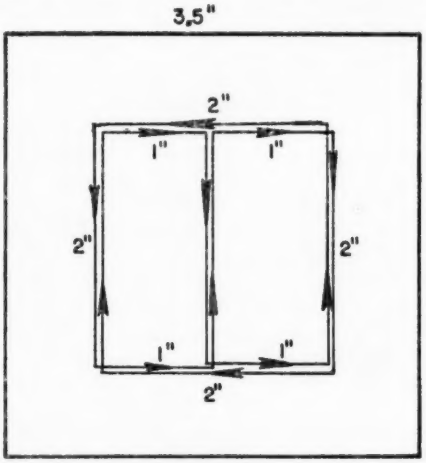


FIGURE 8.—*Direction and magnitude of the transverse motions of the specimen during a test on the Shawmut machine.*

on a side is cut from each of the four corners of this specimen. The resultant specimen, also shown in figure 7, contains a central square, 3½ in. on a side, which is the area tested, and four 1½-in. extensions, one on each side of this square, which are used to fasten the specimen in the special clamps of the machine. The clamps are provided with means for keeping the specimen under tension throughout the test. The clamps and the horizontal platen over which the specimen is stretched are mounted on two horizontal plates, each plate being actuated by a special cam to produce alternate transverse motions at right angles to each other. These motions follow a definite sequence which is repeated after two cycles. The directions and magnitudes of these motions for the two cycles are indicated in figure 8, where the indicated trace shows the motion of the center of the wearing surface relative to the specimen. These motions bring the various

sections underneath the wearing surface, which is parallel to the specimen. This wearing surface, also shown in figure 7, is annular in shape, 2¾ in. outside diameter and ¾ in. inside diameter. It is made of special metal and is very smooth. It contains four radial slots, which are at right angles to each other. The wearing surface is given a reciprocating rotary motion about the vertical axis of the annular disk. The disk is brought to bear against the carpet specimen with a constant force exerted by a dead weight through a lever. A cam lifts the disk from the carpet specimen intermittently. The pile of the specimen is thus subjected to slipping, twisting, and compressive forces which continually change in direction and magnitude, but repeat regularly during the test. The motions of the edges of the radial slots in the wearing surface relative to the pile produce the wear on the specimen. A typically worn-out specimen is also shown in figure 7.

The worn-off material is removed from the specimen during a test by suction, which is applied through the central hole of the wearing disk. The amount of suction is indicated on a gage and may be adjusted to a predetermined value by means of a valve. The debris is collected in a cloth bag.

A mechanism is provided which automatically measures the thickness of the carpet specimen and records it on a chart. The thickness measurements are always made at the same area of the specimen. These measurements may be made at intervals of 5 or 20 minutes. The 5-minute interval is used if the test is completed in less than 15 hours and the 20-minute interval if the duration of the test is more than 15 hours. After a test is started, the machine runs without interruption until it stops automatically, which indicates that the specimen is worn to a predetermined thickness.

The transverse motions of the specimen, the rotary motion of the wearing surface, and the intermittent vertical motion of the disk are produced positively and are therefore maintained constant. The wearing surface remains highly polished and shows no change during the tests. In this test, if the pile of the specimen changes so that the frictional force between the fibers and the wearing surface is increased, then the energy expended on the sample per rotary motion of the wearing surface is increased. This increase in expenditure of energy for each rotary motion of the wearing surface probably explains the excessive heating of the wearing disk during the tests of some of the carpets. This condition usually produced a shimmy motion between the specimen and the wearing surface, and the resultant rate of wear of the specimen was greatly increased. The pile was frequently pulled out bodily, as shown in figure 9.

3. THICKNESS GAGE FOR CARPETS

The thickness gage for measuring the wear of carpets is shown in figure 3. It is provided with a base on which the turntable of the wear-testing machine is mounted, so that the center of the worn track of the specimen is located directly underneath the 1-in. circular foot of the dial micrometer. The foot is fastened to the stem of the dial micrometer with a ball-and-socket connection. A weight is placed on top of the stem to make the pressure which the foot will exert on the specimen equal to 0.75 lb/in^2. The dial-micrometer assembly

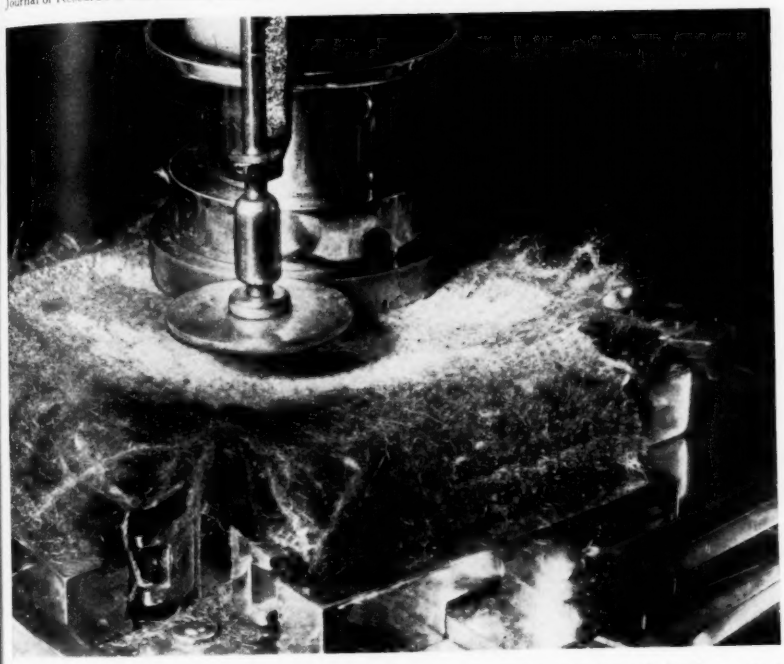


FIGURE 9.—*Appearance of specimen which became excessively heated during a test on the Shawmut machine.*

FIGURE 10.—*Gage for measuring the thickness of the carpets laid in a long corridor for service wear tests.*

FIGURE 11.—*Instrument for measuring the length of a tuft of pile.*

may be moved vertically by means of a rack and pinion. A needle is fastened to this assembly. The point of the needle is in the plane of the bottom surface of the foot when the pointer of the dial micrometer coincides with the zero of the scale. It is apparent that when the dial-micrometer assembly is lowered, the foot will rest on the specimen and exert a pressure of 0.75 lb/in.^{2} and the needle will pierce the carpet until the point comes in contact with the steel plate of the turntable. The distance between the point of the needle and the bottom surface of the foot is equal to the thickness of the carpet. This value is read directly from the dial to the nearest 0.001 in. The turntable may be rotated and the thickness measured at a number of positions around the worn track.

The entire gage mounting may be rotated through 180°, and the thickness of carpets which are laid on hard-surfaced floors may be measured. Figure 10 shows the instrument being used for thickness measurements of carpets laid in a long corridor. A mirror mounted in front of the dial greatly facilitates reading of the scale when these thickness measurements are made.

4. INSTRUMENT FOR MEASURING THE LENGTH OF A TUFT OF PILE

The instrument for measuring the length of a tuft of pile yarn taken from a sample of carpet is shown in figure 11.[4] The instrument is provided with two interchangeable brass plates. Each plate contains two V-shaped slots. The base angle of each slot is 60°. The four slots are of different sizes, the widths across the top equalling 0.150, 0.125, 0.100, and 0.050 in., respectively. The largest slot is used for measuring very coarse pile yarns and the smallest slot for measuring very fine pile yarns or the plies of a coarse pile yarn. The other two slots are for yarns of intermediate sizes. A plate is inserted in the instrument with the slot of appropriate size in the front position, directly underneath a wide-field lens having a magnification of about 5 diameters. A glass plate on which is reproduced a scale, 1.5 in. long and graduated in 0.01 in., fits over the slot. The scale is on the bottom surface of the glass plate to minimize the effect of parallax. The scale is illuminated by a small lamp. The U-shaped tuft to be measured is picked up with tweezers at the bottom of the U, the glass scale is tilted up at the front, and the two ends of the tuft are inserted into the V-slot. The tuft is readily straightened by applying a slight force with the tweezers. The glass scale is lowered, which further straightens the tuft and presses it slightly into the V-slot. The tuft is then released, and the tweezers are withdrawn through a slot and semicircular recess at the front of the plate. The scale is moved horizontally to aline the zero line of the scale with one end of the tuft. The line of the scale which coincides with the other end of the tuft is noted, and the length is recorded to the nearest 0.01 inch. With this instrument the lengths of 100 tufts can be measured in 1 hour with ease. The standard error of 50 measurements was found to be 0.002 inch.

[4] A similar instrument has been described by Hopkins and Dow in Textile World **87**, 1159 (1937).

III. TESTING PROCEDURE

1. ANALYSIS OF CARPET CONSTRUCTION

The number of rows of tufts per inch of length of carpet was determined by counting the rows in 10 in. at three different places, and the pitch, number of tufts per inch of width, was determined by counting the tufts in 10 in. at three different places. The pile height, length of the pile tuft projecting above the back, was measured with a steel scale graduated in 1/64 in. The average of five measurements was taken as the pile height. The tuft length was measured with the instrument described in section II, 4. The average of 50 measurements was taken as the tuft length. These 50 tufts were weighed, and the weight per tuft and the weight of the pile yarn per inch of length were computed. The density of the pile was computed by the expression $2RPW/L$, where R is the number of rows per inch, P is the pitch per inch, W is the weight per tuft in grains, and L is the length of the tuft in inches.

2. THICKNESS

The thickness of the pile of a carpet was obtained by subtracting the thickness of the back of the carpet from the total thickness.

To measure the thickness of the back, a 6- by 10-in. specimen was taken, a flame was directed over the area of the specimen, and the pile was destroyed by alternate charring and brushing without damage to the back. The average of 10 measurements with the instrument described in section II, 3, was taken as the thickness of the back.

The total thickness of a carpet was obtained by measuring a specimen after it was mounted on the turntable. The average of 10 measurements, made at different places around the annular area to be tested for wear, was taken as the total thickness of the carpet. The total thickness and pile thickness of a specimen after it had been subjected to wear on the wear-testing machine were measured in like manner.

3. WEAR OF CARPETS

(a) NBS MACHINE

Unless otherwise noted, the wear tests on the NBS machine were made under the following conditions:

Downward force at each pulley	135 lb
Braking torque	7.5 lb ft
Speed of turntable	80 rpm
Height of suction nozzle above the pile	1/8 in.
Amount of suction	4 cm Hg
Relative humidity of air	65 percent
Temperature of air	70° F

The thickness of the carpet specimen was measured at the beginning of a test and again after 500, 1,000, 2,000, 5,000, 10,000, and after every additional 10,000 revolutions of the turntable. The thickness of the pile was plotted against the number of revolutions of the turntable. A test was discontinued when the plot showed that the pile was worn off. Two or more specimens of each carpet were tested.

(b) SHAWMUT MACHINE

A chart was mounted on the recording drum and reference marks corresponding to zero thickness were recorded. The machine was set to stop when the thickness was equal to the back thickness, previously determined on a specimen of the same carpet. The specimen, already described, was mounted in the machine and its thickness was recorded. The machine was started and the suction was adjusted until the gage indicated a suction of 20 in. of water.[5] The thickness was recorded at regular intervals. The test was continued without interruption until the pile was worn off and the machine automatically stopped.

(c) SERVICE TESTS

The service tests on 24 carpets of different constructions were conducted in the south corridor located on the fifth floor of the Procurement Division Building, Washington, D. C. This location was selected because several thousand people walked through this corridor each day. Each carpet consisted of three strips 27 in. wide and 5 ft. long (see fig. 10). The three strips were sewed together to cover the width of the corridor. The 24 carpets were sewed together to form a strip 120 ft. long. A 5-ft. length of a spare carpet was sewed to each end to absorb any excess wear occasioned at the ends. The carpets were laid in one continuous length over a fairly hard-surfaced floor of asphalt tile. The carpet strip was tacked directly to the floor around the edges. The thicknesses of the carpets were measured on the floor at the beginning of the test and at regular intervals during the test. Thirty measurements were made on each carpet construction. These measurements were spaced approximately 1 ft. along the length and across the width of each carpet. A photoelectric cell counter was installed to count the number of persons walking over the carpets each day. The carpets were cleaned once every day, using the central suction system of the building. The duration of each cleaning period was approximately 45 minutes. Detached vacuum-cleaning units of the rotating brush and agitator types were used during a portion of the duration of the service tests. The amount of dirt removed each day by each of the three cleaning systems was weighed during a test period lasting about 6 months. The service tests were continued for 162 weeks, during which time about 2,000,000 people walked over the carpets. The carpet strips were then washed in a commercial carpet-cleaning plant and each carpet was photographed.

4. WEAR INDICES

The change in thickness of the pile of a carpet during a test has been found to be the best measure of the amount of wear. The curve shown in figure 12 is typical of the change in thickness of the pile that takes place during a laboratory or a service-wear test. The thickness of the pile decreases very rapidly during the early stage of a test. This rapid decrease is caused primarily by a matting of the pile. After the pile has been matted, its thickness decreases at a fairly uniform rate for the remainder of the wear test.

The wear index used in Research Paper RP640,[6] referred to as the *K* index, is defined as the number of thousands of revolutions of the

[5] A mercury manometer probably would perform more satisfactorily than the gage furnished with the machine.

[6] See footnote 1 on p. 334.

turntable required to wear the pile down to one-fourth of its original thickness. This point is marked K in figure 12. It was believed by some members of the carpet industry that the K index did not evaluate all weaves of carpets in the correct relationship, particularly the lower-quality carpets of the Axminster weave. To overcome this criticism, the author suggested a new wear index, referred to as the S index, which is based upon the matted thickness of the pile. The matted thickness is obtained by extrapolating the more or less flat portion of the curve back to the zero of the abscissa scale, shown by

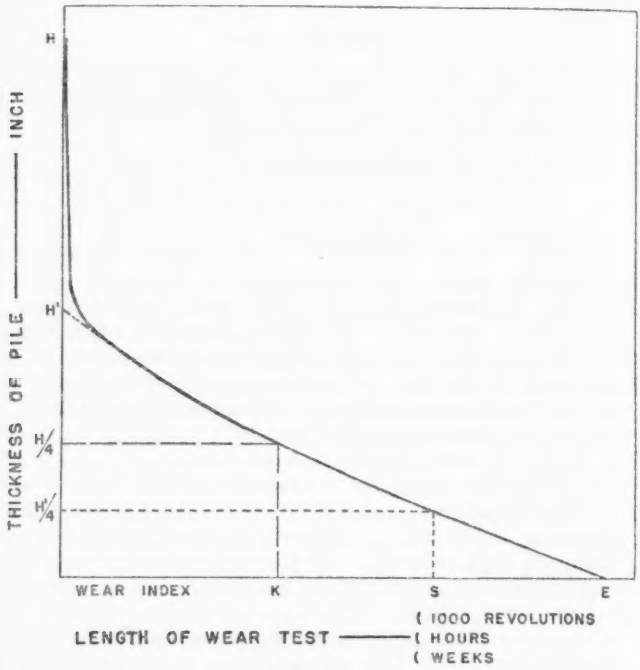


FIGURE 12.—*Typical curve showing the change in thickness of the pile of a carpet during a wear test.*

the broken line in figure 12. The S index is defined as the number of thousands of revolutions of the turntable required to wear the pile down to one fourth of its matted thickness. This point is marked S in figure 12. Another wear index which has been proposed is the number of thousands of revolutions of the turntable required to wear the pile down to zero thickness. This wear index is known as the E index and is marked E in figure 12. The unit for these wear indices obtained with the Shawmut machine is expressed in hours and the unit for these wear indices obtained in the service tests is expressed in weeks.

IV. MATERIALS TESTED

The carpets for this investigation were furnished by the Bigelow Sanford Carpet Co., the Mohawk Carpet Mills, Inc., and the Alexander Smith & Sons Carpet Co. Some of the carpet series were especially woven according to specified constructions. Several carpets from miscellaneous sources were added to the list. The carpets and pertinent information regarding their construction are listed in table 2.

TABLE 2.—*Analysis of carpets and test results*

Weave [a]	Rows per inch, R	Pitch per inch, P	Weight per tuft, W	Length of tuft, L	Weight of tuft per inch length $B=W/L$	Height of pile,[b] H	Initial thickness of pile [c]	Initial thickness of back [c]	Density of pile, $D=2RPB$	(Density of pile)×(Pile height) DH	(Density of pile)^2×(Pile height) D^2H	S index: NBS machine	S index: Shawmut machine	S index: Service tests
			Grains	*Inches*	*Grains*	*Inches*	*Inches*	*Inches*	*Grains/in.*^{3}	*Grains/in.*^{2}	*Grains*^{2}*/in.*^{3}	1,000 *revolutions*	*Hours*	*Weeks*
Wilton	7.9	9.4	0.097	0.46	0.211	0.17	0.162	0.108	31.3	5.3	167	34	7.6	.....
	8.0	9.4	.097	.51	.190	.19	.174	.108	28.6	5.4	155	43	7.3	.....
	9.9	9.4	.088	.46	.191	.17	.169	.108	35.5	6.0	214	56	9.6	.....
	9.9	9.3	.102	.50	.204	.19	.192	.108	37.6	7.2	269	62	8.9	.....
	11.9	9.4	.093	.47	.198	.17	.187	.108	44.3	7.5	334	87	12.0	.....
	11.8	9.3	.096	.51	.188	.19	.202	.108	41.3	7.8	324	84	11.3	.....
1	8.0	9.3	.091	.48	.189	.17	.170	.105	28.1	4.8	134	39	10.2	205
2	10.0	9.3	.094	.46	.204	.19	.172	.107	37.9	7.2	273	78	12.0	308
3	11.8	9.3	.089	.45	.198	.17	.178	.110	43.5	7.4	322	99	14.8	370
4 [d]	10.0	9.3	.066	.36	.183	.16	.150	.105	34.0	5.4	185	36	9.8	171
5	9.9	9.3	.092	.52	.177	.20	.203	.107	32.6	6.5	213	71	12.5	368
6	9.9	9.3	.108	.57	.189	.23	.225	.107	34.8	8.0	278	74	12.8	398
*Chenille	5.1	10.3	.123	.58	.212	.26	.190	.199	22.3	5.8	129	4.7	.7	.....
	5.2	10.5	.148	.68	.218	.29	.230	.199	23.8	7.0	164	5.6	1.0	.....
	5.1	10.0	.191	.88	.217	.41	.275	.199	22.1	9.1	201	6.0	1.3	.....
	5.9	12.0	.126	.58	.217	.24	.223	.208	30.7	7.4	226	9.4	1.1	.....
	6.0	12.2	.148	.68	.218	.31	.275	.208	31.9	9.9	315	11.7	1.5	.....
	6.0	12.1	.199	.90	.221	.40	.370	.208	32.1	12.8	412	12.1	1.9	.....
	6.8	14.2	.121	.56	.216	.26	.238	.217	41.7	10.9	452	19.7	2.1	.....
	6.9	13.6	.155	.72	.215	.33	.310	.217	40.4	13.3	538	18.8	2.1	.....
	6.8	14.0	.216	.98	.220	.46	.424	.217	41.9	19.3	808	22.5	3.0	.....
Axminster	4.6	7.0	.140	.62	.226	.20	.116	.133	14.5	2.9	42	6.6	2.8	.....
	4.6	7.1	.187	.84	.223	.28	.150	.133	14.6	4.1	60	6.9	1.4	.....
	5.4	7.0	.137	.64	.214	.19	.119	.146	16.2	3.8	61	8.4	1.5	.....
	5.4	7.0	.192	.86	.223	.28	.187	.146	16.9	4.7	80	12.3	2.0	.....
	7.3	7.0	.139	.64	.217	.20	.174	.140	22.2	4.4	99	21.3	3.9	.....
	7.3	7.0	.186	.85	.219	.28	.262	.140	22.4	6.3	140	24.8	2.8	.....
	9.1	7.0	.138	.62	.223	.22	.188	.140	28.3	6.2	176	30.3	4.0	.....
	9.0	7.0	.195	.85	.229	.31	.305	.140	28.9	9.0	259	40.3	4.2	.....
14	4.2	7.0	.171	.86	.199	.33	.151	.125	11.6	3.8	44	5.6	1.5	65
13	4.4	7.1	.173	.87	.199	.33	.139	.125	12.4	4.1	51	8.0	3.5	70
12	4.7	7.0	.175	.84	.208	.33	.146	.130	13.5	4.5	60	8.8	2.8	80
11	4.8	7.0	.175	.85	.206	.33	.164	.130	13.8	4.6	63	11.6	3.8	102
8	6.2	7.0	.167	.86	.194	.33	.212	.135	16.8	5.5	93	22.0	7.2	152
10	8.0	7.0	.196	.87	.225	.33	.295	.135	25.2	8.3	210	44.2	10.0	260
9	6.1	7.0	.133	.65	.205	.23	.160	.135	17.5	4.0	70	21.8	6.4	114
7	6.1	7.0	.210	1.04	.202	.42	.285	.135	17.3	7.3	126	23.2	7.9	220
	8.9	7.2	.117	.48	.244	.22	.178	.108	31.3	6.9	216	75	13.5	.....
	8.9	7.2	.131	.50	.234	.25	.198	.108	30.0	7.5	225	81	14.8	.....
	8.9	7.2	.141	.54	.235	.28	.259	.108	31.4	8.8	276	103	15.5	.....

Velvet, plain	8.9	7.2	.117	.48	.244	.22	.178	.108	31.3	6.9	236	75	13.5	
	8.9	7.2	.131	.56	.254	.25	.198	.108	30.9	7.5	225	81	14.8	
	8.9	7.2	.102	.66	.245	.28	.259	.108	31.4	8.8	276	103	15.5	
	8.9	7.2	.228	.89	.256	.41	.363	.108	32.8	13.5	441	121	18.0	
	8.9	7.9	.119	.48	.247	.20	.187	.108	34.7	6.9	241	97	17.5	
	8.9	7.9	.136	.55	.247	.25	.213	.108	34.7	8.7	301	104	16.5	
	8.9	7.9	.162	.63	.257	.28	.262	.108	36.1	10.1	365	125	19.0	
	8.9	7.9	.233	.90	.259	.41	376	.108	36.4	14.9	543	168	23.0	
15	6.1	8.0	.121	.50	.247	.16	.130	.110	24.1	3.9	93	40	5.3	110
16	7.1	8.0	.118	.48	.246	.16	.135	.110	27.9	4.5	124	54	6.2	169
17	8.1	8.0	.113	.47	.240	.17	.144	.110	31.1	5.3	164	65	7.9	171
18	9.1	8.0	.115	.47	.245	.17	.160	.110	34.9	5.9	207	82	7.0	245
19	10.0	8.0	.116	.48	.242	.19	.163	.110	38.7	7.4	285	120	8.0	230
20	8.0	8.0	.091	.37	.246	.13	.120	.110	31.5	4.1	129	54	6.5	140
21	8.1	8.0	.107	.42	.255	.14	.135	.110	33.0	4.6	152	62	6.9	162
22	8.1	8.0	.143	.56	.255	.22	.187	.110	33.0	7.3	240	69	7.4	239
23	8.1	8.0	.157	.65	.242	.25	.218	.110	31.4	7.9	246	75	7.3	280
24	8.1	8.0	.194	.78	.249	.33	.265	.110	32.3	10.7	344	80	8.0	304
A	9.1	7.1	.134	.55	.244	.22	.200	.108	31.5	6.9	218	65	10.2	
B	9.1	7.1	.131	.53	.247	.22	.200	.108	31.9	7.0	224	61	11.8	
C	9.1	7.1	.145	.53	.274	.22	.208	.108	35.4	7.8	276	88	14.5	
D	9.1	7.1	.140	.52	.269	.22	.211	.108	34.8	7.7	266	78	13.8	
E	9.1	7.1	.139	.54	.258	.22	.211	.108	33.3	7.3	244	84	15.2	
F	9.1	7.1	.145	.52	.279	.22	.211	.108	36.1	7.9	287	85	13.5	
Velvet, twisted pile	7.5	7.7	.154	.44	.350	.16	.128	.112	40.4	6.5	261	43	6.8	
	8.5	7.7	.153	.45	.340	.19	.133	.119	44.5	8.5	376	61	6.2	
	9.6	7.6	.155	.45	.344	.19	.147	.121	50.2	9.5	480	89	7.7	
	7.5	7.7	.178	.51	.349	.20	.164	.112	40.3	8.1	325	50	6.4	
	8.6	7.6	.181	.51	.355	.22	.164	.119	46.4	10.2	474	66	7.2	
	9.6	7.6	.184	.53	.347	.22	.185	.121	50.6	11.1	564	96	8.3	
	7.6	7.7	.213	.60	.355	.22	.206	.112	41.5	9.1	379	49	7.1	
	8.6	7.6	.206	.61	.338	.25	.211	.119	44.2	11.1	488	68	8.2	
	9.6	7.6	.218	.61	.357	.25	.227	.121	52.1	13.0	679	86	8.4	
	7.5	7.7	.233	.67	.348	.31	.242	.112	40.2	12.5	501	54	6.1	
	8.6	7.6	.235	.66	.356	.31	.239	.119	46.6	14.5	673	69	8.1	
	9.7	7.6	.234	.67	.349	.31	.259	.121	51.4	16.0	820	96	8.6	

See footnotes at end of table.

TABLE 2.—*Analysis of carpets and test results*—Continued

Weave [a]	Rows per inch, R	Pitch per inch, P	Weight per tuft, W	Length of tuft, L	Weight of tuft per inch length $B=W/L$	Height of pile,[b] H	Initial thickness of pile [c]	Initial thickness of back [c]	Density of pile, $D=2RPB$	(Density of pile)×(Pile height) DH	(Density of pile)²×(Pile height) D^2H	S index: NBS machine	S index: Shawmut machine	S index: Service tests
			Grains	*Inches*	*Grains*	*Inches*	*Inches*	*Inches*	*Grains/in.³*	*Grains/in.²*	*Grains²/in.⁵*	*1,000 revolutions*	*Hours*	*Weeks*
Velvet, printed	7.0	8.0	0.199	0.58	0.343	0.25	0.223	0.128	38.4	9.6	369	71	[d]3.0	
	7.0	8.0	.287	.82	.350	.34	.339	.128	39.2	13.3	522	92	[d]2.2	
	7.0	8.0	.358	.94	.381	.39	.390	.128	42.7	16.7	711	105	[d]3.3	
	8.9	7.9	.194	.58	.335	.25	.230	.133	47.1	11.8	554	149	[d]3.3	
	8.9	8.0	.298	.85	.351	.34	.358	.133	50.0	17.0	850	172	[d]5.6	
	8.9	7.9	.324	.95	.341	.41	.416	.133	47.9	19.6	941	171	[d]7.4	
	9.0	8.0	.151	.42	.360	.19	.175	.110	51.8	9.9	510	[e]	18	
	9.1	8.0	.153	.42	.364	.19	.171	.110	53.0	10.1	534	[e]	[d]6	
	9.0	8.0	.150	.40	.375	.19	.176	.110	54.0	10.3	554	[e]	15.8	
	9.0	8.0	.134	.45	.298	.16	.170	.115	42.9	6.9	295	[e]	14.0	
	9.0	8.0	.141	.45	.313	.16	.167	.115	45.1	7.2	325	[e]	14.3	
	9.0	8.0	.137	.45	.304	.16	.168	.115	43.8	7.0	307	[e]	16.0	
	9.0	8.0	.139	.45	.309	.16	.170	.115	44.5	7.1	317	[e]	17.0	
	9.0	7.9	.206	.57	.361	.23	----	.125	51.4	11.8	608	[e]	11.1	
	9.0	8.0	.191	.57	.335	.23	----	.125	48.2	11.1	534	[e]	15.3	
	8.9	8.0	.196	.56	.350	.23	----	.125	49.8	11.5	570	[e]	13.3	
	9.0	8.0	.188	.57	.330	.23	----	.125	47.5	10.9	519	[e]	[d]7.6	
	9.0	8.0	.188	.57	.330	.23	----	.125	47.5	10.9	519	[e]	[d]7.1	
	9.3	7.9	.213	.65	.328	.25	.268	.109	48.4	12.1	586	137	17.0	
	8.0	8.0	.112	.49	.229	.16	.165	.107	29.3	4.7	137	40	12.8	
	9.3	7.9	.197	.65	.303	.27	.261	.102	44.5	12.0	534	96	17.4	
	9.3	7.9	.221	.69	.320	.25	.228	.133	47.0	11.8	552	260	8.0	
	9.1	7.9	.243	.71	.342	.27	.257	.125	49.2	13.3	654	262	12.3	
	[f]7.8	7.8	.163	1.09	.150	.41	.212	.113	18.2	7.5	136	171	6.2	
	[g]4.7	7.0	.169	.70	.241	.25	.164	.133	15.9	4.0	64	20	2.0	
	[f]7.0	6.7	.720	1.21	.595	.47	.400	.115	55.8	26.2	1463	73	10.0	
	12.0	9.3	.082	.44	.186	.19	.161	.110	41.5	7.9	327	68	[d]6.0	
	8.4	7.8	.137	.56	.245	.22	.194	.132	32.1	7.1	227	.63	12.5	
Miscellaneous	9.1	7.3	.134	.55	.245	.22	.184	.111	32.4	7.1	231	81	14.0	
							.440	.133				124	20.0	
							.250	.142				318	17.0	
							.237	.105				154	10.0	
							.274	.140				47	7.0	
							.274	.115				90	8.0	
							.286	.115				140	[d]3.0	
							.257	.115				75	13	
							.300	.110				68	12	
												134	(?)	

						.257	.115				75	13
						.300	.110				68	12
						.562	.103				111	(f)
						.499	.155				150	(f)
						.318	.108				155	14.5
						.260	.108				197	[e] 3.0
						.308	.088				91	9.5

[a] Numerals indicate the number designation of the service-wear tests. Capital letters indicate a series of carpets in which 20 percent of various wastes were added to the base blend of the pile used in carpet *A*.

[b] Measured with a steel scale.

[c] Measured with a gage having a circular foot 1 in. in diameter and exerting a pressure of 0.75 lb/in.^{2}

[d] Two-shot construction.

[e] Excessive heating and shimmying were produced in the test with the Shawmut machine.

[f] Not tested.

[g] Jute pile.

[h] 50 percent of rayon and 50 percent of wool pile.

[i] Twisted pile.

[j] The wool forming the pile of the chenille carpets showed serious degradation according to the alkali-solubility test. This degradation of wool and the low wear indices which were obtained is *not* typical of commercial production of chenille or other carpets. The results for these chenille carpets are included in this paper because they do furnish an excellent example of the definite relationship which exists between the wear test results and the chemical degradation of the wool forming the pile of a carpet.

V. STANDARDIZATION OF TEST ON NBS MACHINE

1. EFFECT OF BRAKING TORQUE, DOWNWARD FORCE AT EACH PULLEY, AND SPEED OF TURNTABLE

The effects of varying the braking torque, downward force at each pulley, and the speed of the turntable on the wear of carpets were reported in Research Paper RP315.[7] It was found that fixed values must be set for these quantities, and these values must be maintained constant during each test in order to effect standardization of the test. The values for these quantities which are given in section III, 3a, are based upon these tests.

2. EFFECT OF RELATIVE HUMIDITY AND TEMPERATURE

Tests, to show the effect of relative humidity and temperature of the air with which the carpet specimens are in equilibrium during the wear test on the NBS machine were made in the laboratories of the

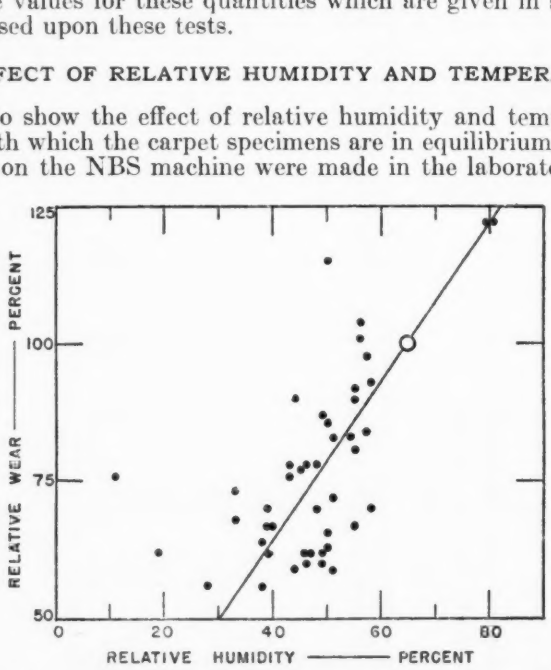


FIGURE 13.—*Effect of relative humidity on the relative wear of carpets.*

Bigelow Sanford Carpet Co., the Mohawk Carpet Mills, Inc., the Alexander Smith & Sons Carpet Co., and the United States Testing Co. The results of the tests at different relative humidities are shown graphically in figure 13, where the relative wear of the carpets in percent is plotted against the relative humidity. The relative wear of each carpet tested is taken to be 100 percent when tested at a relative humidity of 65 percent. The results show that the relative wear increases significantly with the relative humidity. A 10-percent change in relative humidity from 65 percent corresponds to a 15-percent change in the relative wear of the carpets. The data regarding the effect of the temperature of the air on the relative wear of carpets are rather meager. The relative wear of a carpet appears to decrease as the temperature of the air is increased. It is thus important that the wear tests of carpets be made in an atmosphere of controlled temperature and relative humidity.

[7] See footnote 1 on p. 334.

3. EFFECT OF HEIGHT OF NOZZLE AND SUCTION AT THE NOZZLE

Twelve carpets were tested to show the effects of the height of the nozzle above the pile and of the amount of suction at the nozzle. The wear indices of these carpets increased an average of 3 percent when the height was decreased from ⅛ to 1/16 in. This increase results from less effective cleaning because of the decrease in the volume of air entering the nozzle as it is lowered from ⅛ to 1/16 in. The wear indices increased an average of 75 percent when the height was increased from ⅛ to ⅜ in. This large increase is attributed to ineffective cleaning at the ⅜-in. height. These results indicate that the optimum height of the nozzle above the pile is between ⅛ and 1/16 in. The wear indices increased an average of 24 percent when the suction was decreased from 4 to 2 cm Hg. This increase is attributed to less effective cleaning at the lower suction. It is apparent that the height of the nozzle above the pile and the amount of suction must be maintained at fixed values. Obviously the dimensions of the opening of the nozzle and the position of the suction connection relative to the opening of the nozzle must also be fixed to effect standardization of the test with this machine.

VI. RESULTS

1. WEAR INDICES

The cumulative frequencies, in percentages, of the deviations of the individual wear tests for the K, S, and E indices obtained with the NBS and Shawmut machines are given in table 3. The deviation of a test from the average of several tests on the carpet includes the variation between the specimens tested, the experimental errors in singeing the pile from a carpet specimen and in measuring the back thickness, in measuring the total thickness of a carpet before and during a wear test, in obtaining the matted pile thickness by extrapolation of the wear curve, and in operating the wear-testing machines, and small changes in atmospheric conditions. In view of these different errors which enter in the measurement of the wear of a carpet, it seems rather remarkable that the deviation of a single wear test is less than 10 percent in 9 trials out of 10. On the basis of the frequency distributions of the deviations for the three wear indices, it is concluded that the S index is more reliable than either the K or the E index. This conclusion applies to both the NBS and the Shawmut machines. The larger deviation for the K index probably results because the initial pile thickness, which enters in this index, varies more between specimens because of partial matting of the pile in the handling of the carpet after manufacturing. The initial pile thickness as measured by the Shawmut machine is uncertain, for it is based upon one measurement only and it is also greatly influenced by the mounting of the specimen in the machine. The larger deviation for the E index probably results because of the uncertainty of determining the point of intersection of the pile thickness curve with the abscissa axis. This determination frequently involves some extrapolation of the curve, which becomes nearly paralled to the axis at the end of a test.

487101—42——4

TABLE 3.—*Cumulative frequencies, in percentages, of deviations of the individual wear tests for the K, S, and E indices obtained with the NBS and Shawmut machines*

[The deviation of a test on a carpet is expressed as a percentage of the average of two or more tests on the carpet]

Deviation	Cumulative frequency					
	NBS wear indices [a]			Shawmut wear indices [b]		
	K	*S*	*E*	*K*	*S*	*E*
Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
0	11	10	11	12	13	9
1	25	27	19	20	23	23
2	35	38	38	26	36	38
3	47	45	48	36	48	51
4	59	53	61	42	61	62
5	65	63	65	55	70	71
6	75	77	75	58	77	78
7	79	79	79	64	81	80
8	85	87	83	69	86	83
9	89	88	83	75	90	86
10	89	91	89	78	93	90
11	93	94	90	81	95	92
12	95	97	93	82	97	95
13	97	98	94	86	98	96
14	97	100	95	90	98	96
15	97	----	95	90	98	97
16	98	----	95	90	99	97
17	98	----	96	92	99	97
18	98	----	97	94	99	98
19	98	----	97	95	99	99
20	98	----	98	97	100	100
21	98	----	98	97	----	----
22	98	----	98	97	----	----
23	99	----	98	98	----	----
24	99	----	98	98	----	----
25	99	----	98	99	----	----
26	99	----	98	99	----	----
27	100	----	98	100	----	----
28	----	----	98	----	----	----
29	----	----	99	----	----	----
30	----	----	100	----	----	----

[a] The NBS results are based upon 179 tests on 85 carpets, 2.1 tests per carpet.
[b] The Shawmut results are based upon 210 tests on 86 carpets, 2.4 tests per carpet.

The relationship between the *S* index and the *K* and *E* indices is shown in figures 14, 15, and 16 for the NBS, Shawmut, and service tests, respectively. A good linear relationship is shown between the indices, although the points are scattered considerably more for the Shawmut machine. The effect of the greater matting of the jute and of the part-rayon-pile carpets is indicated by the NBS machine but not by the Shawmut machine. On the average a test would have to be continued 40 percent beyond the *S* index to obtain the *E* index on the NBS machine. The prolongations for the Shawmut and service tests are 100 and 35 percent, respectively. These prolongations of the tests do not seem justified in view of the good linear relationship between the *S* and *E* indices. On the other hand, the prolongation of a test to obtain the *S* index compared with the *K* index, amounting to 20, 50, and 45 percent of the *S* index for the NBS, Shawmut, and service tests, respectively, can be justified because of the increase in the precision of the results and also, as shown in the next section, because the *S* index of the service tests corresponds

more nearly with the time at which a carpet would be discarded on account of visible wear.

2. SERVICE TESTS

Photographs of the middle strip of the carpets after 162 weeks of

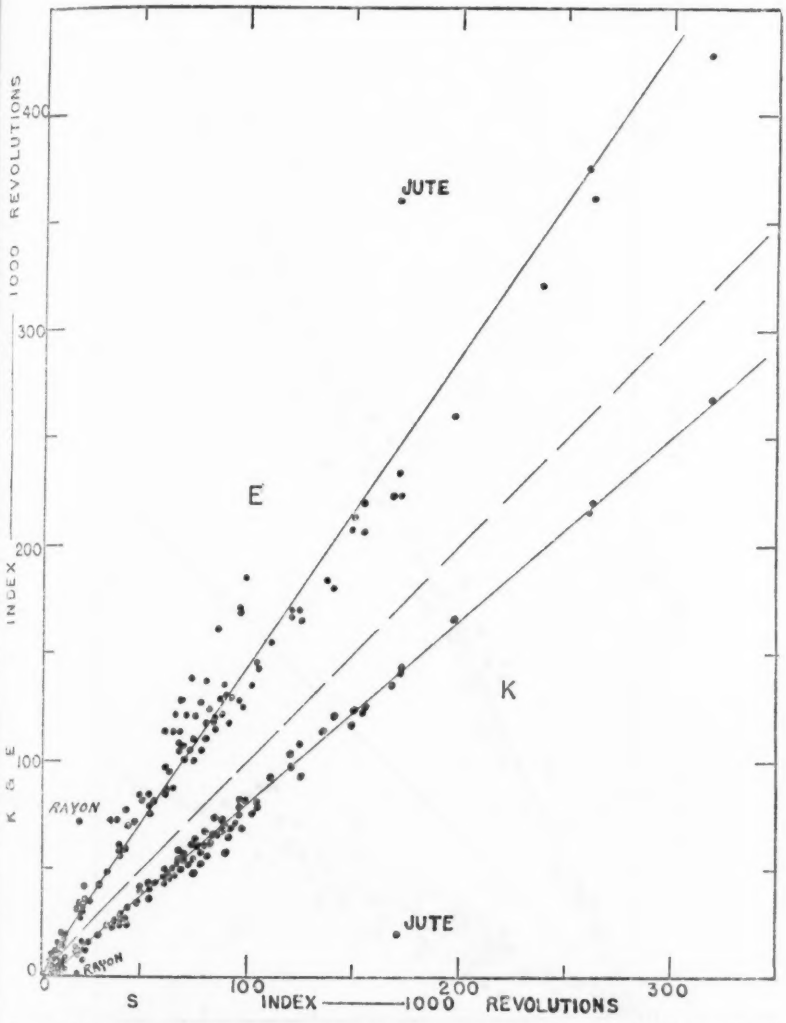


FIGURE 14.—*Relationship between S and K and E indices of carpets obtained with the NBS machine.*

service wear, followed by washing in a commercial carpet-cleaning plant, are shown in figures 17 to 29, inclusive. The photographs and the discussion of the measurements of thickness of the carpets are confined to the middle strip because it received more uniform wear.

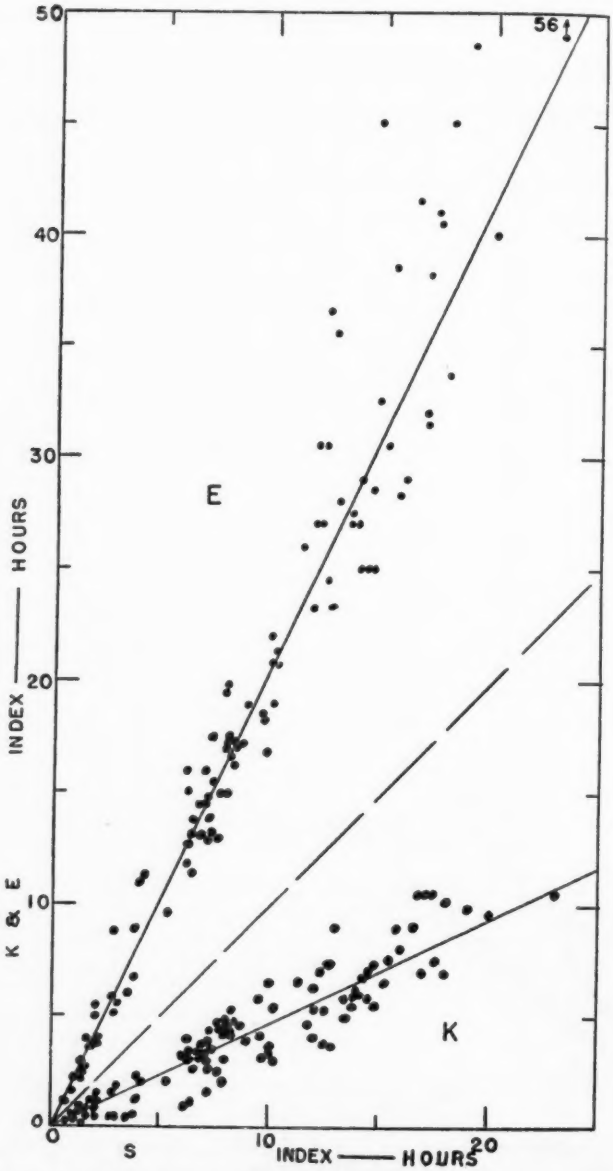


FIGURE 15.—*Relationship between S and K and E indices of carpets obtained with the Shawmut machine.*

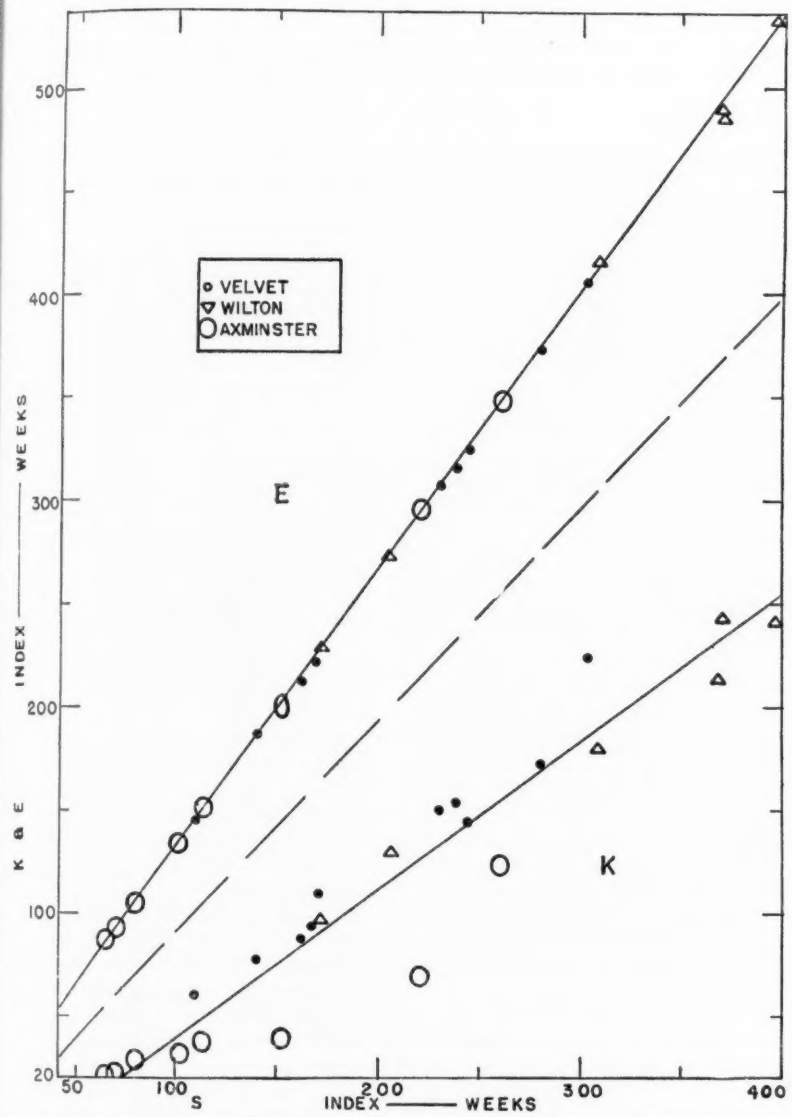


FIGURE 16.—*Relationship between S and K and E indices of carpets obtained in the service wear tests.*

The outside edges of the side strips showed in general less wear because the traffic was definitely less along the walls of the corridor. A few carpets showed more wear in one of their outside strips because of the increased traffic in front of doorways. The influence of this increased traffic extends to the middle strip of carpets 15 and 21 and probably also affected the middle strip of carpet 19. Carpet 4 (fig. 23) contains an area which appears like a stain. This condition was caused by the pile matting in different directions, often called pile crushing. It occurred during the first few weeks of the service tests and persisted throughout the investigation. The change in appearance is still very pronounced at the end of 162 weeks of wear and after the washing of the carpet.

Five technical men of the carpet industry examined the carpets at the end of the 162-week test period. According to their judgment, carpets 14, 13, 12, 11, 15, 9, 20, 21, and 16 should have been discarded at some earlier time. Carpets 8, 17, 4, and 1 had been worn to such a degree that they should have been discarded. The remaining 11 carpets had sufficient pile left to be continued in use. The judgment of these technical men agrees quite well with the S index based upon the measurements made during the service tests. The carpets are listed in table 4 according to the magnitude of the S index of the service tests. The K and E indices are given for comparison, together with notes made by the author as the service tests progressed.

If it is assumed that a carpet should be discarded when it shows noticeable general wear, then the remarks given in table 4 may be used to express this condition numerically in terms of weeks of service wear. These values, termed visual wear indices, are plotted as ordinates in figure 30, using the S indices of the service tests as abscissas. It will be noted that the points plotted for the 14 worn-out carpets fall into two groups, one for the Axminster carpets and the other for the velvet and Wilton carpets. The relationship between the visual and the S indices for each group is represented fairly well by a straight line. The visual wear index for the Axminster group averages about 20 percent higher than the S index. The opposite is true for the velvet and Wilton group, for which the visual wear index averages about 25 percent lower than the S index. In other words, according to the S index, the Axminster carpets would be discarded prematurely, whereas the velvet and Wilton carpets would be discarded too late. This apparent difference arises because no allowance was made in the calculation of the S index for a decrease in back thickness of the carpets which occurred during the service test. This decrease in the back thickness is much greater for the Axminster carpets than for the velvet and Wilton carpets. It depends upon the type of weave and also upon the firmness of the back construction for a given weave. It is estimated that the back thickness of carpet 14 decreased about 33 percent during the 162 weeks of the service tests. This estimate is based on the total thickness of carpet 14 at the end of 157 weeks, which was 0.087 in., and the initial back thickness, which was 0.125 in. This estimate is probably low as there was still some pile remaining at the end of 162 weeks, as is shown in figure 17. If an allowance is made for this decrease in the back thickness, the corrected S index is about 125 instead of 65 weeks. If this value is plotted against the visual wear index of 90 weeks in figure 30, the point falls very

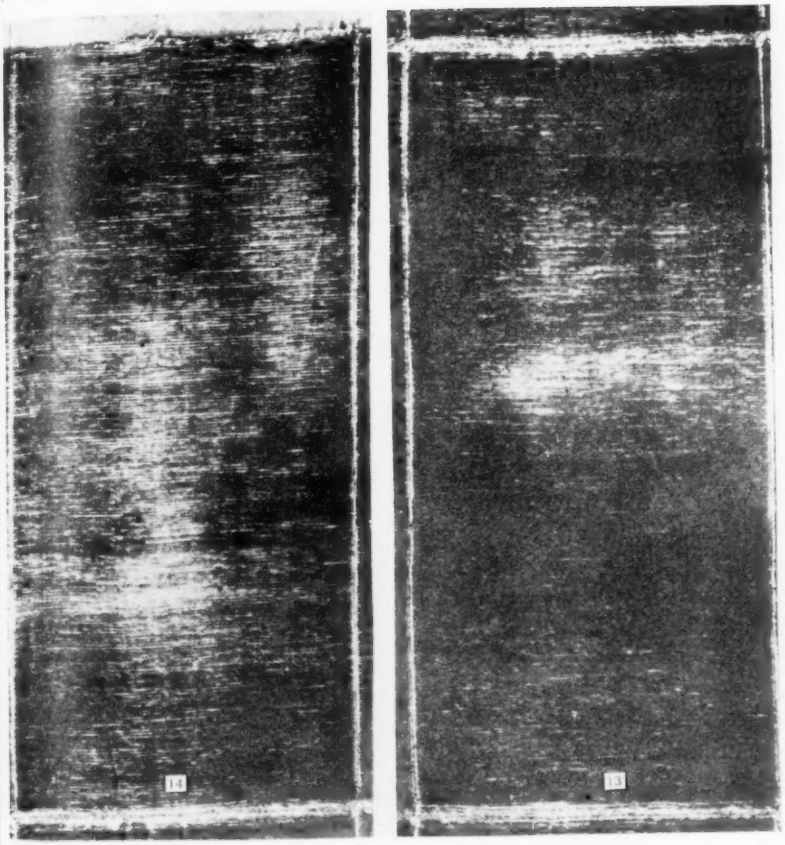


FIGURE 17.—*Carpets 14 and 13 after 162 weeks of service wear; S indices, 65 and 70 weeks, respectively.*

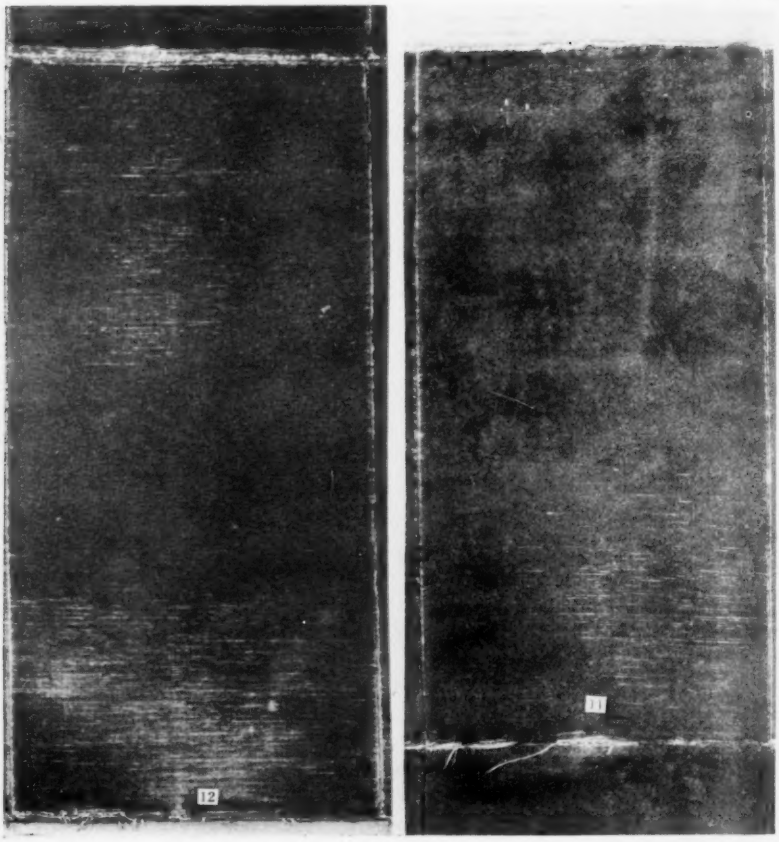


FIGURE 18.—*Carpets 12 and 11 after 162 weeks of service wear; S indices, 80 and 102 weeks, respectively.*

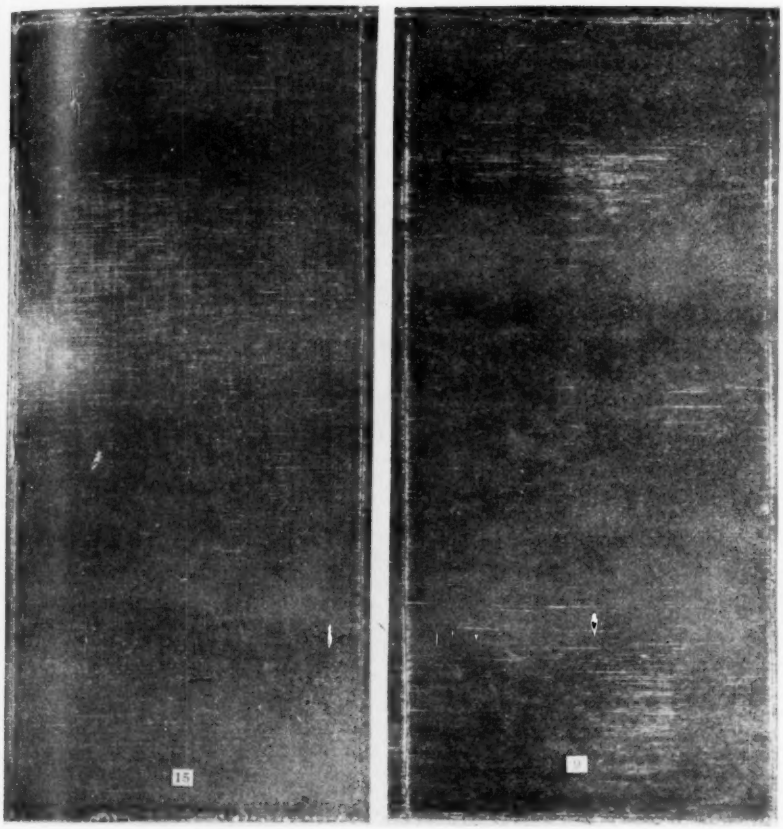


FIGURE 19.—*Carpets 15 and 9 after 162 weeks of service wear; S indices, 110 and 114 weeks, respectively.*

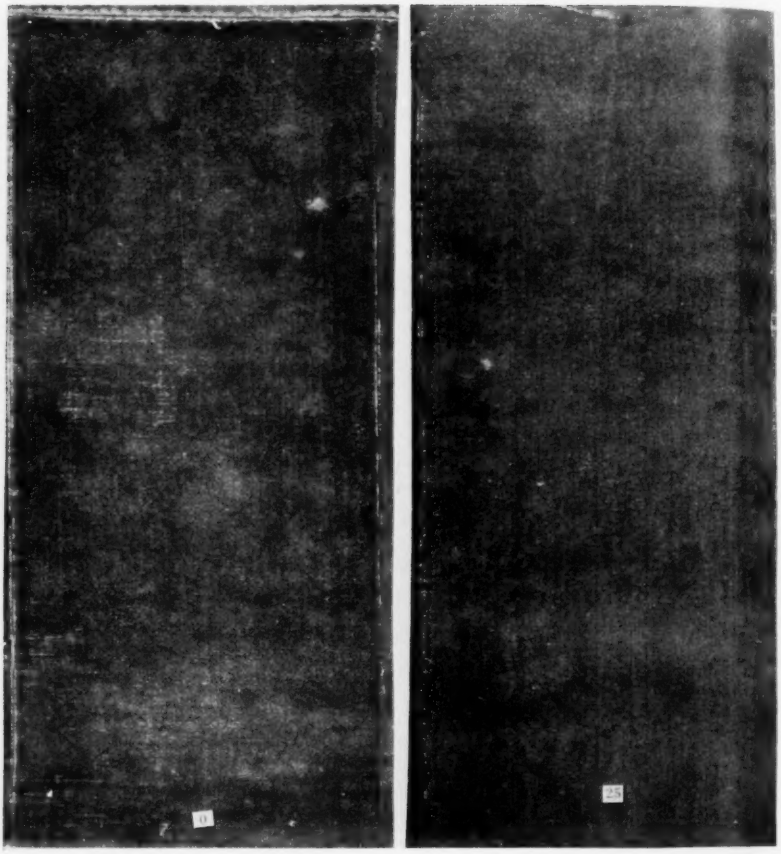


FIGURE 20.—*Carpets 0 and 25 after 162 weeks of service wear; S indices, 138 and 150 weeks, respectively.*

Carpet 0 was located at the east end of the corridor and carpet 25 was located at the west end.

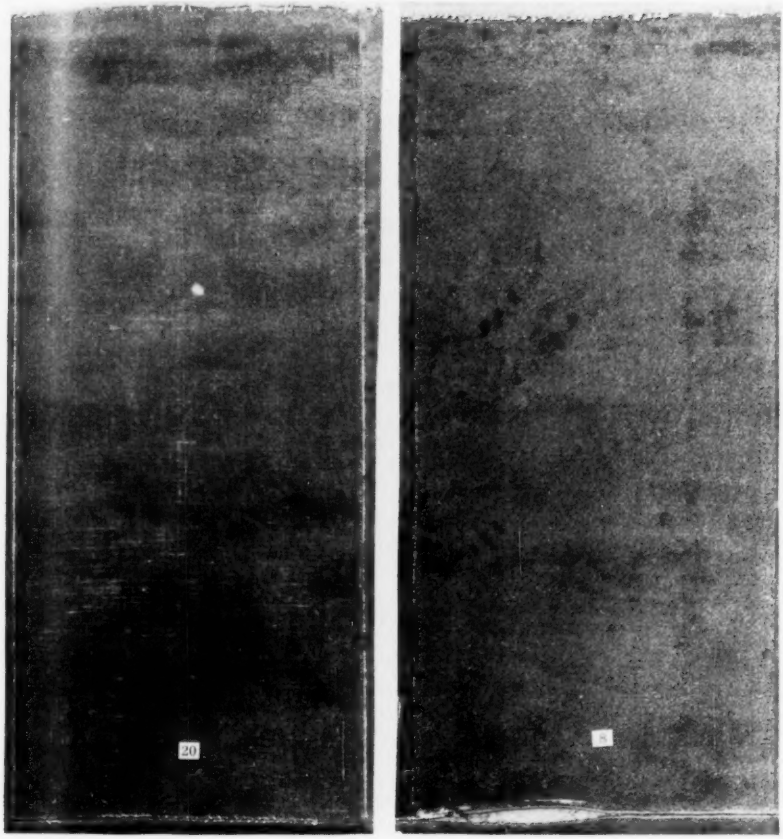


FIGURE 21.—*Carpets 20 and 8 after 162 weeks of service wear; S indices, 140 and 152 weeks, respectively.*

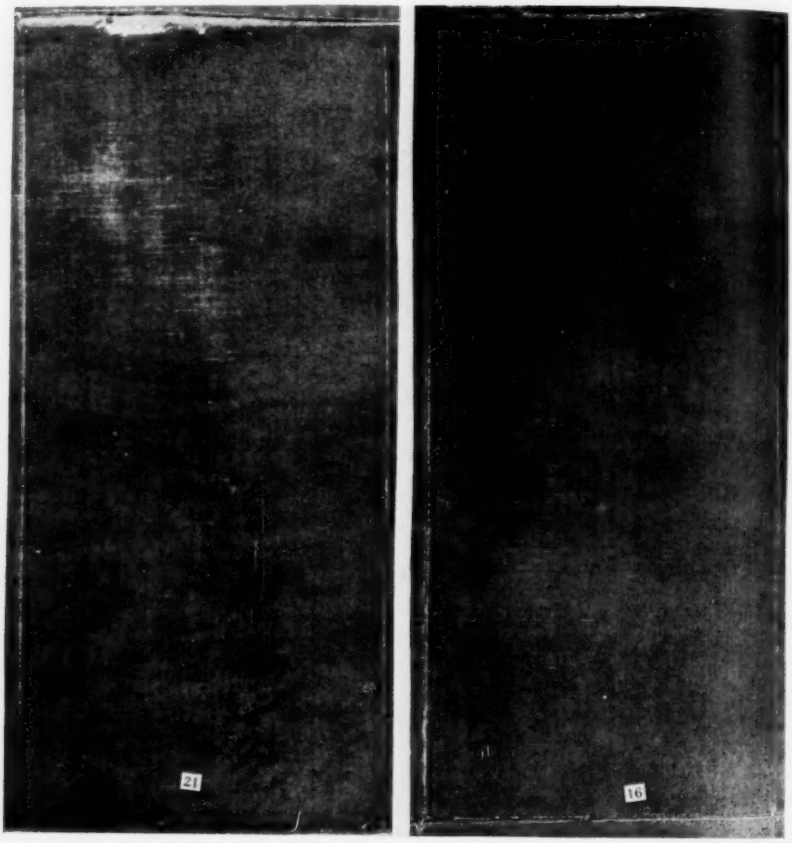


FIGURE 22.—*Carpets 21 and 16 after 162 weeks of service wear; S indices, 162 and 169 weeks, respectively.*

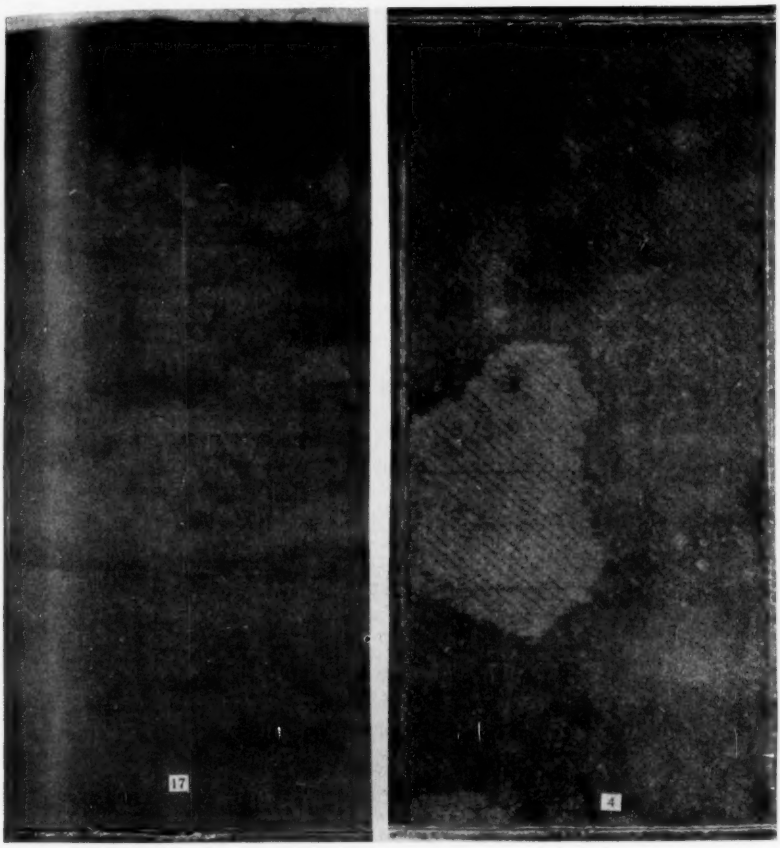


FIGURE 23.—*Carpets 17 and 4 after 162 weeks of service wear; S indices, 171 and 171 weeks, respectively.*

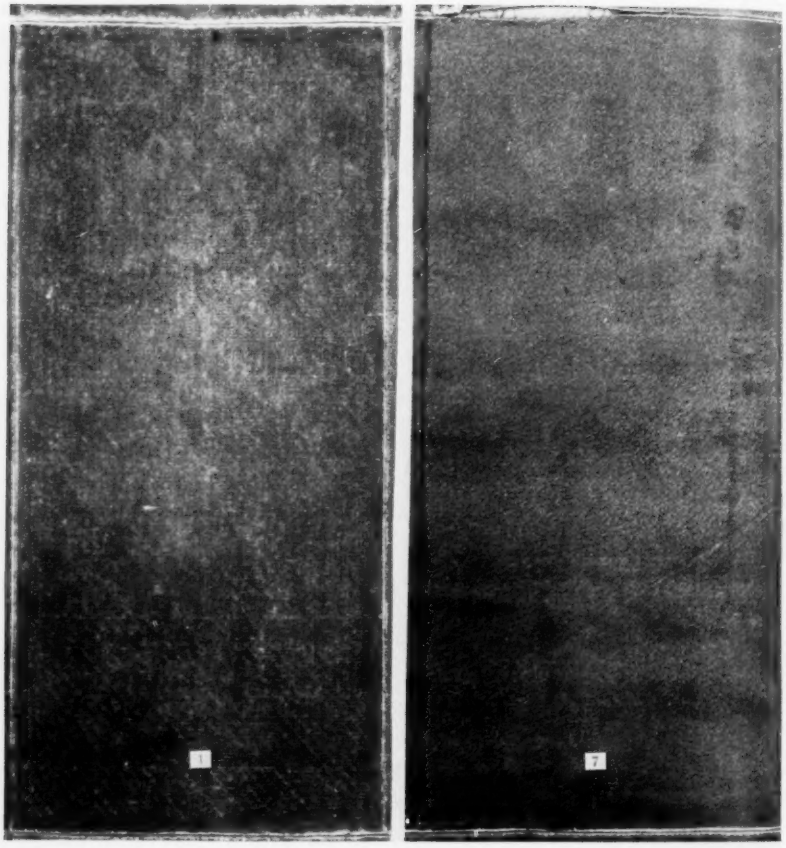


FIGURE 24.—*Carpets 1 and 7 after 162 weeks of service wear; S indices, 205 and 220 weeks, respectively.*

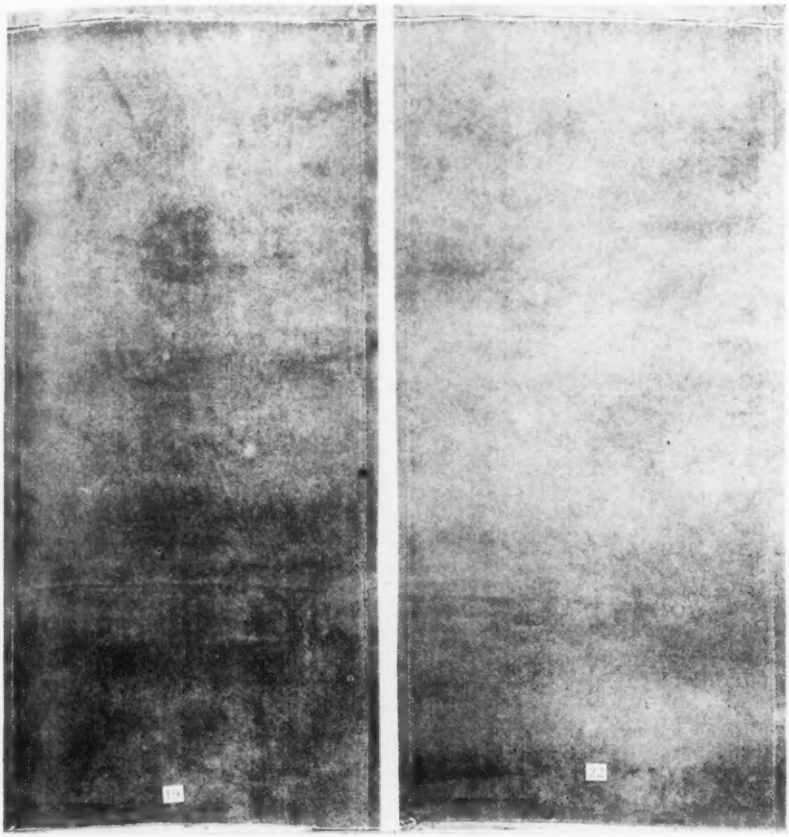


FIGURE 25.—*Carpets 19 and 22 after 162 weeks of service wear; S indices, 230 and 239 weeks, respectively.*

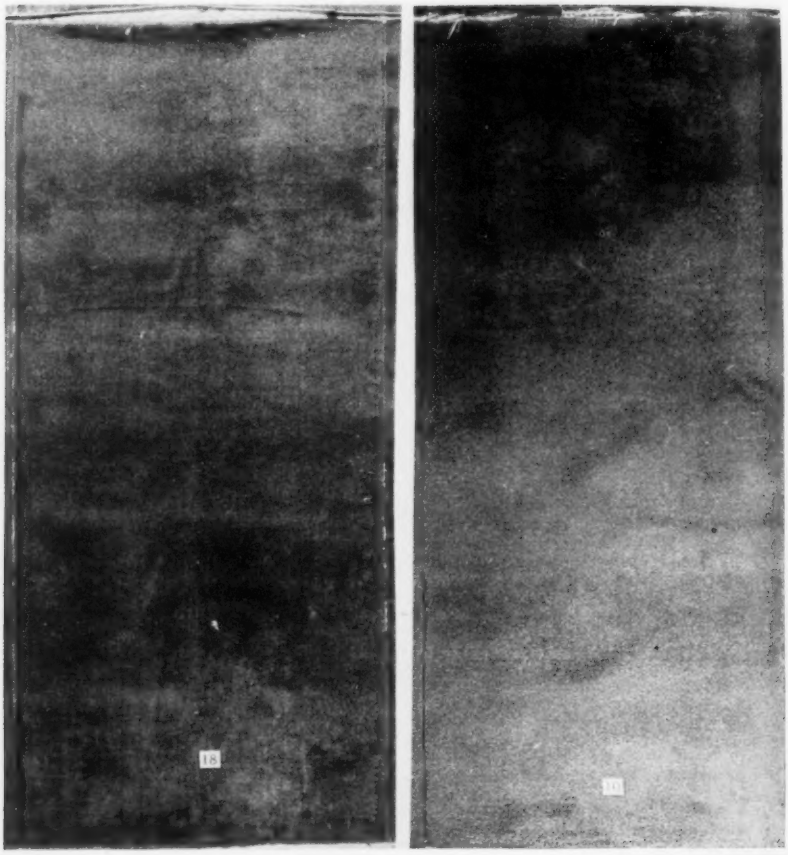


FIGURE 26.—*Carpets 18 and 10 after 162 weeks of service wear; S indices, 245 and 260 weeks, respectively.*

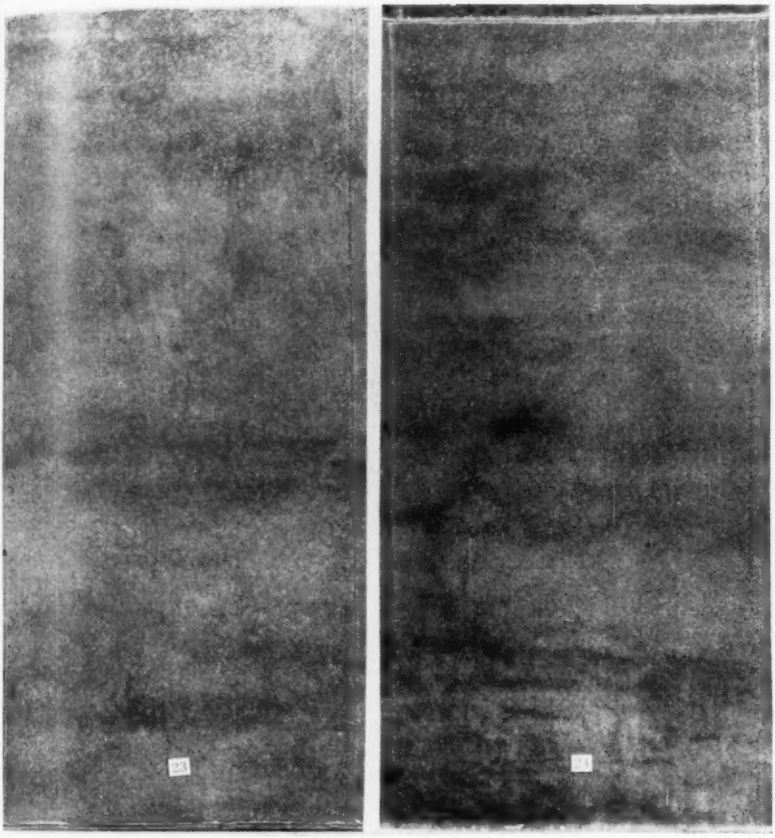


FIGURE 27.—*Carpets 23 and 24 after 162 weeks of service wear; S indices, 280 and 304 weeks, respectively.*

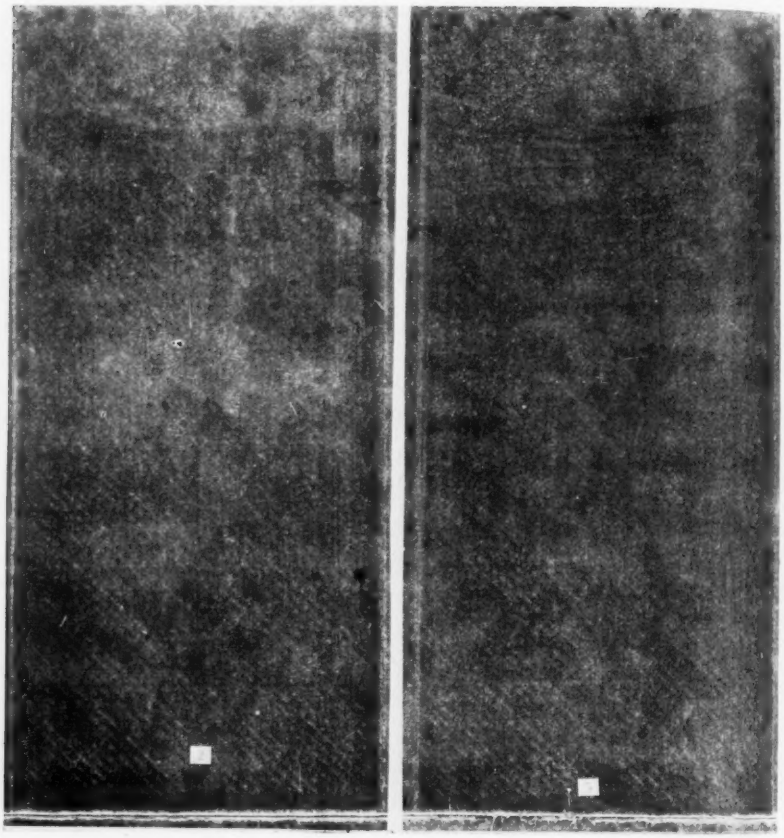


FIGURE 28.—*Carpets 2 and 5 after 162 weeks of service wear; S indices, 308 and 368 weeks, respectively.*

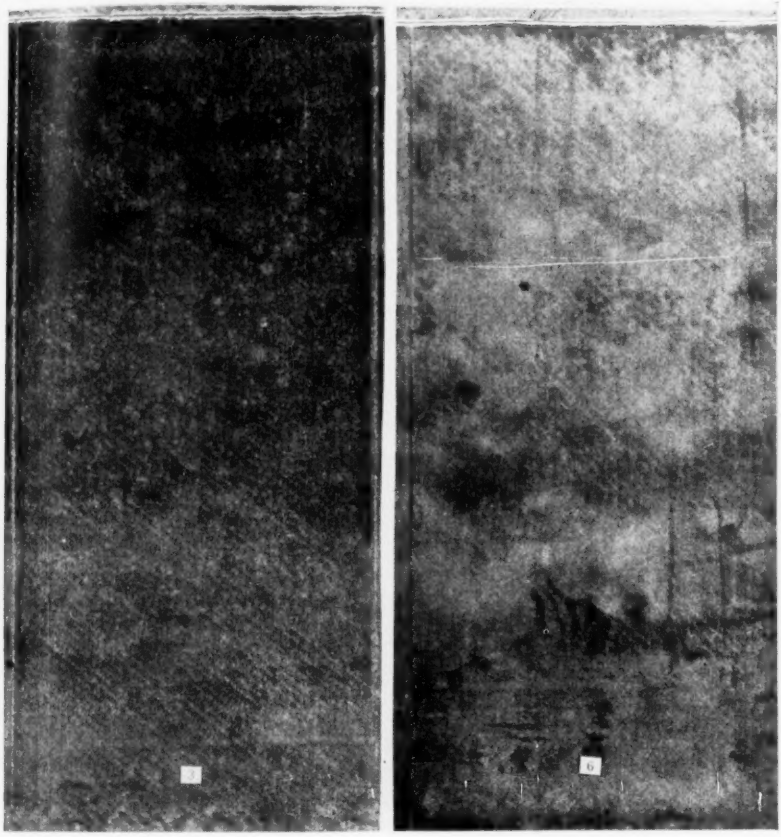


FIGURE 29.—*Carpets 3 and 6 after 162 weeks of service wear; S indices, 370 and 398 weeks, respectively.*

UNIV. OF MICH.

nearly on the straight line for the velvet and Wilton group. If similar allowances are made for carpets 13 and 12, the corrected S indices

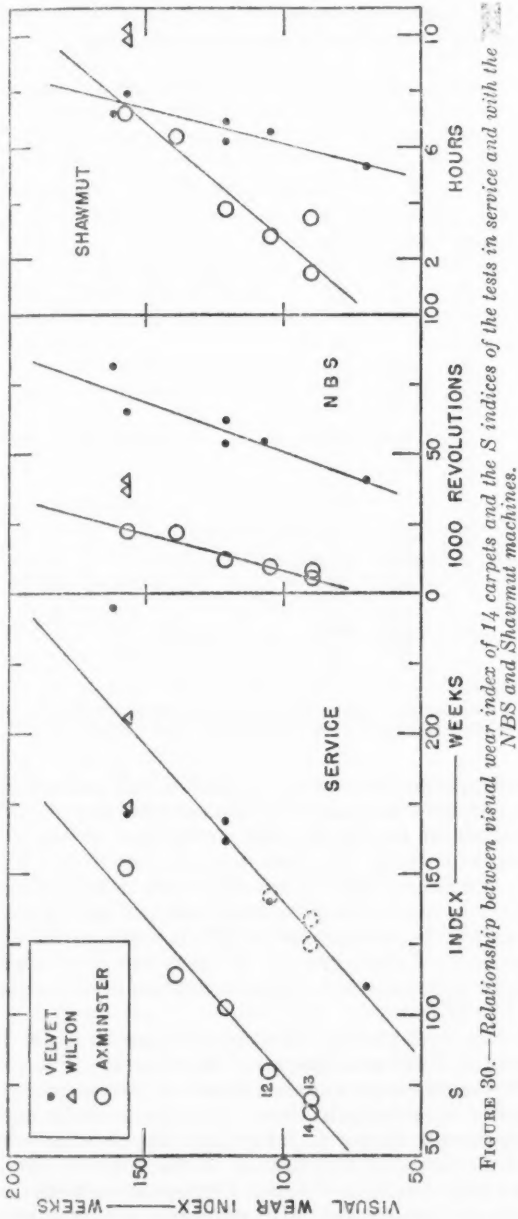


FIGURE 30.—*Relationship between visual wear index of 14 carpets and the S indices of the tests in service and with the NBS and Shawmut machines.*

become about 130 and 150, respectively, instead of 70 and 80 weeks. The points for these values also fall very nearly on the straight line

for the velvet and Wilton groups. This separation of the carpets into two groups may be attributed, therefore, to the decrease in the back thickness of the Axminster carpets. Unfortunately this decrease could not be evaluated during the service tests, so that a true correction cannot be applied to the thickness measurements.

TABLE 4.—*Results of service wear tests on 24 carpets*

Carpet	Service wear index			Remarks after the following weeks of service wear [a]						
	S	*K*	*E*	70	90	105	121	139	157	162 (washed)
	Weeks	*Weeks*	*Weeks*							
14	65	22	87	*s*	*S, g*	*S, G*	*S, G*	*S, G*	*S, G*	*S, G*
13	70	24	93	*s*	*s, g*	*S, G*	*S, G*	*S, G*	*S, G*	*S, G*
12	80	30	106	*s*	*s*	*s, g*	*S, G*	*S, G*	*S, G*	*S, G*
11	102	32	135	.....	.....	*s*	*S, G*	*S, G*	*S, G*	*S, G*
15	110	60	145	*s, g*	*S, g*	*S, G*	*S, G*	*S, G*	*S, G*	*S, G*
9	114	38	151	.....	.....	.....	*s*	*s, g*	*S, G*	*S, G*
20	140	78	187	*s*	*S*	*S, g*	*S, g*	*S, G*	*S, G*	*S, G*
8	152	39	200	.....	.....	.....	*s*	*s*	*S, g*	*S, g*
21	162	88	213	*s*	*s*	*s*	*S, g*	*S, G*	*S, G*	*S, G*
16	169	94	222	.....	*s*	*s*	*S, g*	*S, G*	*S, G*	*S, G*
17	171	110	227	.....	.....	.....	*s*	*s*	*S, g*	*S, G*
4	171	98	228	*c*	*c*	*c*	*c, s*	*c, s*	*c, s, g*	*c, S, G*
1	205	130	272	.....	.....	.....	.....	*s*	*s, g*	*S, g*
7	220	70	295	.....	.....	.....	.....	.....	*s*	*s*
19	230	150	307	.....	.....	.....	.....	.....	*s*	*s*
22	239	154	316	.....	.....	.....	*s*	*s*	*s*	*s*
18	245	144	324	.....	.....	.....	*s*	*s*	*S*	*S, g*
10	260	124	348	*c*	*c*	*c*	*c*	*c, s*	*c, s*	*c, s*
23	280	172	372	.....	.....	.....	*s*	*s*	*s*	.....
24	304	224	406	.....	.....	.....	*s*	*s*	*s*	.....
2	308	180	415	.....	.....	.....	.....	.....	*s*	*s*
5	368	214	490	.....	.....	.....	.....	.....	.....	*s*
3	370	244	485	.....	.....	.....	.....	.....	.....	*s*
6	398	241	533	.....	.....	.....	.....	.....	.....	.....

[a] The symbols have the following meanings: *c* indicates crushing of the pile in different directions; *s* and *S* indicate noticeable and pronounced wear along the seam: and *g* and *G* indicate noticeable and pronounced general wear.

If the visual indices are plotted against the *K* indices of the service tests of these carpets, the points again fall into two groups. Correcting the *K* indices of the Axminster group for the decrease in back thickness does not bring the two groups together. The corrected results of the Axminster group are still very much too small. This difference is attributed to the greater amount of initial matting for the Axminster group, which averaged 0.122 in., compared with 0.076 in. for the velvet and Wilton group. It may be concluded, therefore, that the *S* index gives a much better measure of the relative wear of carpets than the *K* index.

The visual wear index is also plotted in figure 30 against the *S* index of the tests on the NBS and Shawmut machines. The results for the Axminster and velvet carpets again fall into separate groups, each group being represented by a straight line. Since practically no compression of the backing occurs during a test on the Shawmut machine, the two groups cannot be brought together as in the service tests. Although the thickness of the backing of some Axminster carpets decreased considerably during a test on the NBS machine, a correction for this decrease also does not bring the two groups into coincidence. The ex-

planation for the difference between the Axminster and velvet carpets is not apparent but presents a very puzzling problem. It could be assumed that the results of the service tests of the velvet carpets were low because the amount of traffic was greater than for the Axminster carpets. However, since the difference in wear of the two strips at the ends of the corridor was very slight, the *S* indices being 138 and 150 weeks (fig. 20), this explanation does not seem very probable. Localized variation in traffic along the length of the corridor, due to doorways and other causes, can be ruled out as a contributing cause, since there is little scattering of the points for either the velvet or the Axminster groups in figure 30. The difference in wool blend, dyeing, and yarn structure between the carpets of the Axminster and velvet weaves should have the same effect on the visual wear index and on the *S* index of the laboratory tests, unless these factors greatly influenced the appearance of the carpets during the service tests. Appearance is, of course, not taken into consideration when the wear index is based upon thickness measurements. A difference in the nature of the wear on the fibers during the laboratory tests is another factor which could contribute to the observed difference.

3. COMPARISON OF SERVICE, NBS, AND SHAWMUT TESTS ON 24 CARPETS

The *S* index of the service tests of 24 carpets is plotted against the *S* index of the tests on the NBS machine in figure 31. The over-all correlation if fair. The correlation for the carpets of each weave is good, with the carpets of each weave forming a distinct group. The Wilton group falls between the Axminster and velvet groups. The lines for the three groups are nearly parallel and intercept the coordinate axes near the origin.

The *S* index of the service tests is also plotted against the *S* index of the tests on the Shawmut machine in figure 31. The over-all correlation is fair. The correlation for the carpets of each weave is good, with the carpets of each weave forming a distinct group. The lines for the Wilton and velvet groups are nearly parallel, but their intercepts with the coordinate axes are not near the origin. The slope of the line for the Axminster group is, however, very different and the intercepts of the line with the coordinate axes are near the origin.

The *S* index of the tests on the NBS machine is plotted against the *S* index of the tests on the Shawmut machine in figure 32. The over-all correlation is poor. The correlation for the carpets of each weave is good, with the carpets of each weave forming a distinct group. The lines for the Wilton and velvet groups are nearly parallel, but their intercepts with the coordinate axes are not near the origin. The slope of the Axminster group is, however, very different, and the intercepts of the line with the coordinate axes are near the origin.

The relative wear of these carpets when tested on the Shawmut and NBS machines depends very greatly upon some factor which is different for the three weaves. In addition to the fundamental differences between the three weaves, the carpets of one weave probably differ from those of another weave in wool blend, dyeing, and yarn structure, since the carpets of each weave were made by a different manufacturer. It is likely that these factors influence the results differently in each of the three types of tests. The present data are not sufficient to permit a detailed study of this problem.

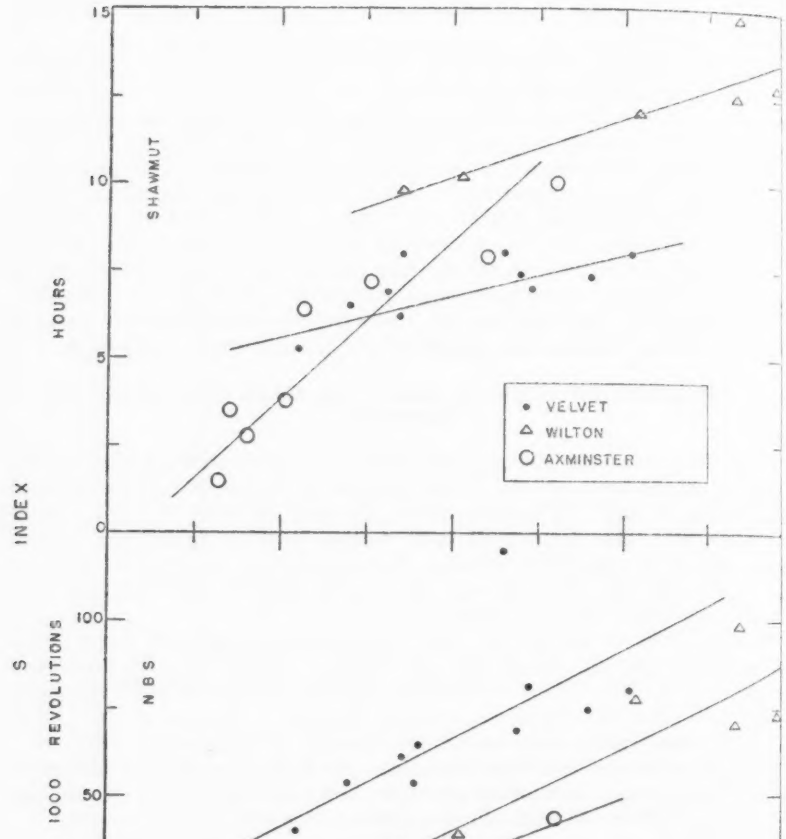


FIGURE 31.—*Relationship between the S index of 24 carpets of the service tests and the S indices of the tests with the NBS and Shawmut machines.*

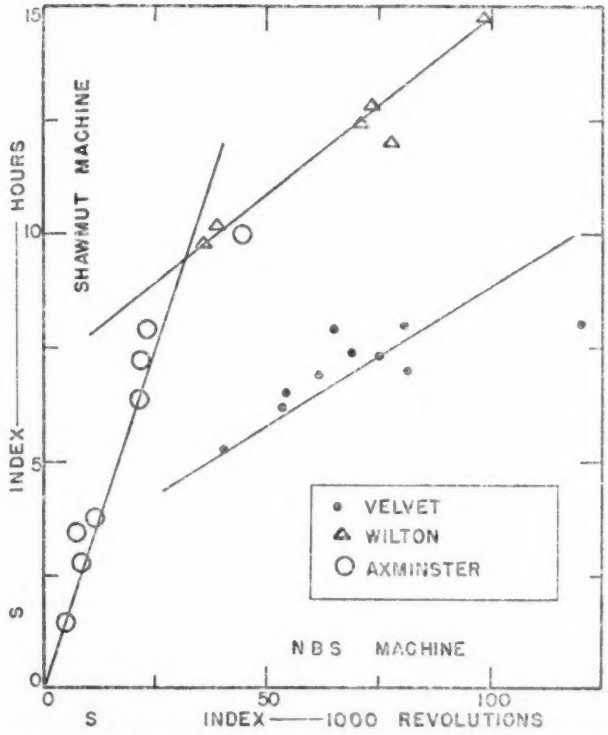


FIGURE 32.—*Relationship between the S indices of 24 carpets tested with the NBS and Shawmut machines.*

4. COMPARISON OF WEAR TESTS WITH ANALYSES OF CARPETS

The products D^2H and DH, where D and H are the density and height of pile, respectively, have been used as a criteria of the relative wear of carpets. The S index of the service tests is plotted against D^2H and DH in figure 33. The S indices of the tests on the NBS and Shawmut machines are similarly plotted in figure 33. The correlation of the S indices with D^2H is good. There is some indication, however, that the correlation is affected by the type of weave or more likely by the wool blend used in the carpets of the three weaves. The correlation of the S indices with DH is also good, although the straight lines do not pass through the origin. There is again some indication that the correlation is affected by the type of weave, wool blend, dyeing, and yarn structure. A more thorough discussion of these factors is given in section 8.

The 24 carpets of Wilton, velvet, and Axminster weaves were made in two series for each weave. In one series all the manufacturing details were kept constant except that the wire height (pile height) was varied systematically. In the other series, all the manufacturing details were kept constant except that the number of rows per inch (tufts per square inch) was varied systematically. The effect of an increase in pile height or in number of tufts per square inch may thus be evaluated.

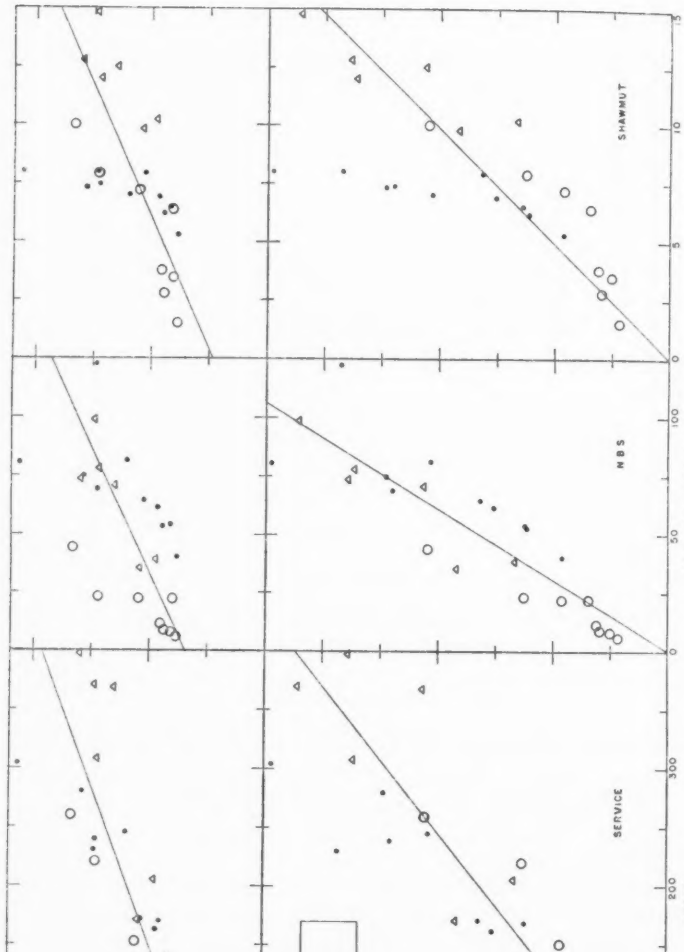


FIGURE 33.—*Relationship between the S indices of 24 carpets and the products D²H and DH, where D and H are density and height of pile, respectively.*

The percentage increase in the S index of the service, NBS and Shawmut tests is plotted in figure 34 against the percentage increase in pile height. The points belonging to the same series are connected by straight lines. An increase of 100 percent in pile height produces an increase of about 75 percent in the S index of the service tests. The corresponding increases in the S indices for the tests on the same carpets with the NBS and Shawmut machines are only 25 and 15 percent, respectively. The laboratory wear tests apparently underestimate the effect of an increase in the height of the pile on the wear of the carpets.

The percentage increase in the S index of the service, NBS and Shawmut tests is also plotted in figure 34 against the percentage increase

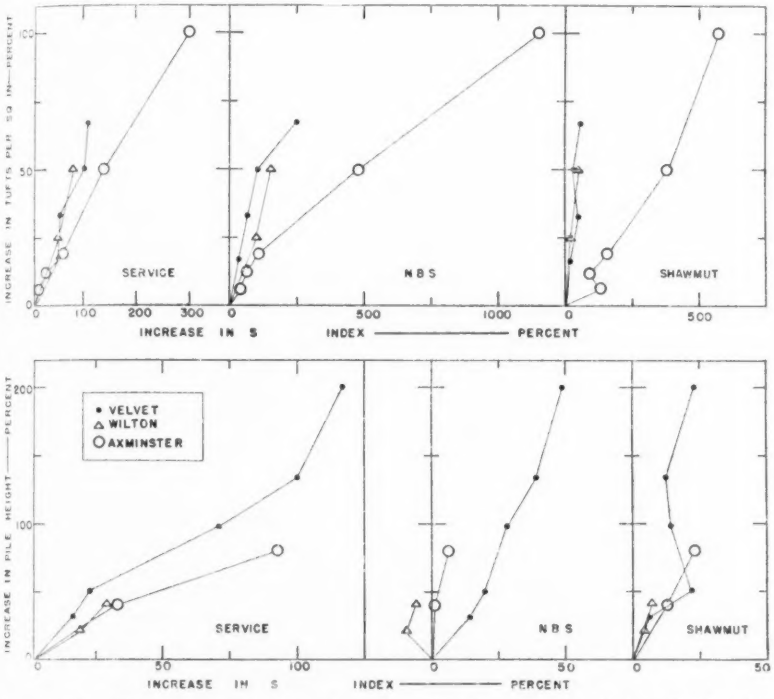


FIGURE 34.—*Effect of pile height and number of tufts per square inch on the S index.*

in number of tufts per square inch. The points belonging to the same series are connected by straight lines. An increase of 100 percent in the number of tufts per square inch produces an increase of about 225 percent in the S index of the service tests. This increase is three times the increase obtained for an increase of 100 percent in height of pile. The increases in the S indices for the tests on the same carpets with the NBS and Shawmut machines depend very much upon the weave. The increase obtained with the Shawmut machine is about 100 percent for the Wilton and velvet weaves and about 600 percent for the Axminster weave. The increase obtained with the NBS machine is about 250 percent for the Wilton and velvet weaves

and about 800 percent for the Axminster weave. The laboratory tests are probably unduly severe on carpets of low quality, and this may account for the large increase obtained for the Axminster carpets, since the percentage increases were computed on the basis of the S index of an Axminster carpet of very low quality.

5. INTERLABORATORY TESTS

The 24 carpets which were subjected to service tests were also tested with the NBS machine in the laboratories of the Mohawk Carpet Mills,

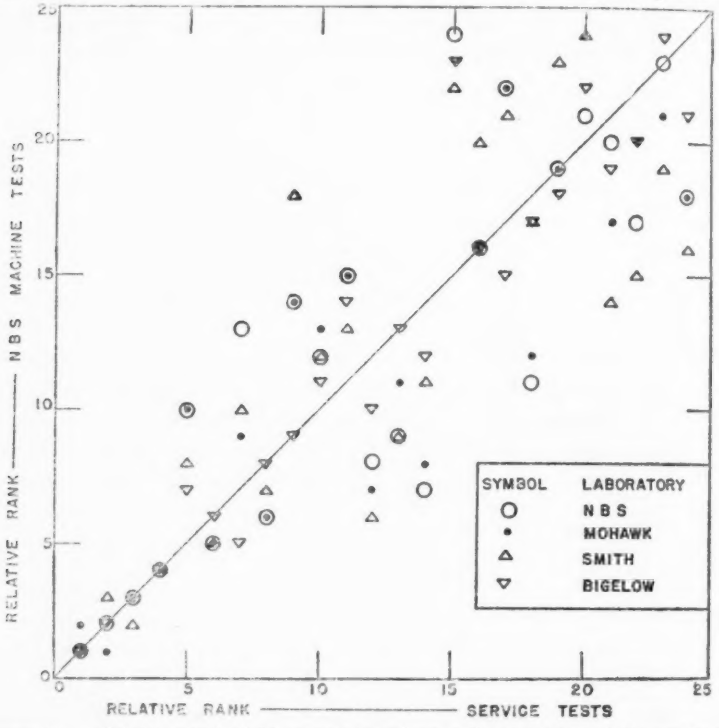


FIGURE 35.—*Relative rank of 24 carpets based upon the S indices of the service tests and the tests on four NBS machines.*

Inc., the Alexander Smith & Sons Carpet Co., and the Bigelow Sanford Carpet Co., and with the Shawmut machine, in the laboratories of the Alexander Smith & Sons Carpet Co. and the Bigelow Sanford Carpet Co. Using the S index of the service test as a basis for arranging the carpets in a relative order, the Kendall rank correlation coefficients were computed for each laboratory and test method. These coefficients ranged in value from 0.62 to 0.85 for the NBS machine and from 0.71 to 0.78 for the Shawmut machine. The corresponding coefficients for D^2H and DH were 0.78 and 0.71, respectively. All these coefficients show a highly significant correlation with the S index of the service tests. The relative rank of the 24 carpets according to the S index of the tests with the NBS machine in the different

laboratories is plotted in figure 35 against the relative rank according to the S index of the service tests. Figures 36 and 37 give similar data for the Shawmut machine and carpet analysis, respectively. It is apparent from these figures that the general correlation of the relative rank of the carpets tested in the laboratories with the relative rank of the carpets of the service tests is very good.

Although the results obtained by the different laboratories apparently evaluated the carpets in much the same relative order as the service test, the numerical values which were obtained differed greatly. These differences are shown by the ratios of the results obtained at

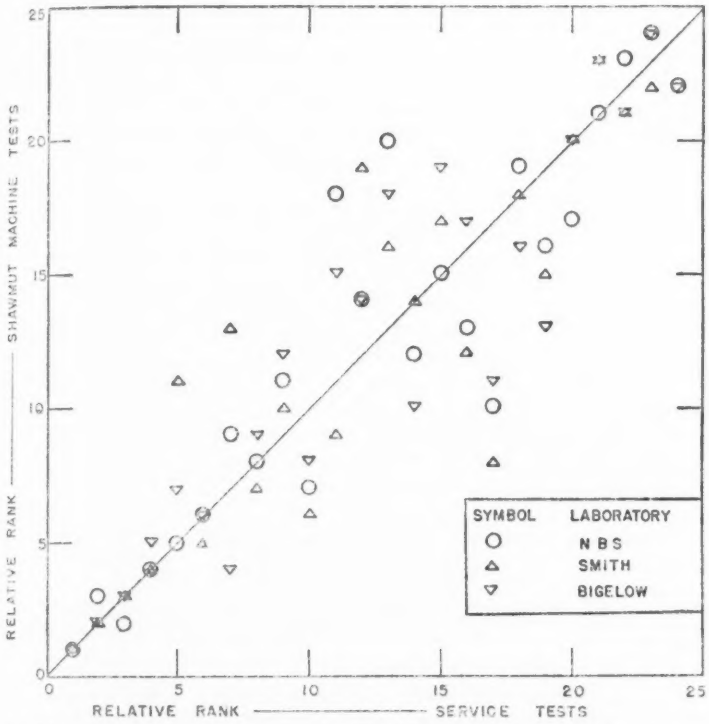


FIGURE 36.—*Relative rank of 24 carpets based upon the S indices of the service tests and the E indices of the tests on three Shawmut machines.*

the National Bureau of Standards to the results obtained in each of the cooperating laboratories. The average ratio and coefficient of variation for each laboratory and testing machine are given in table 5. The large systematic differences obtained with the NBS machine are probably due to a lack of uniformity in the testing procedure. The tests at the National Bureau of Standards were carried to completion on each sample tested; that is, each test was continued until the pile was worn off. This procedure was not followed generally in the cooperating laboratories. If a test is discontinued too soon and the wear indices are arrived at by extrapolation of the wear-test curve, then values which are too low will be obtained. The testing procedure in

this respect varied less in the case of the Shawmut machine, since this machine is set to stop automatically when the thickness of the carpet is reduced to its back thickness. The closer agreement between laboratories for this machine is apparent.

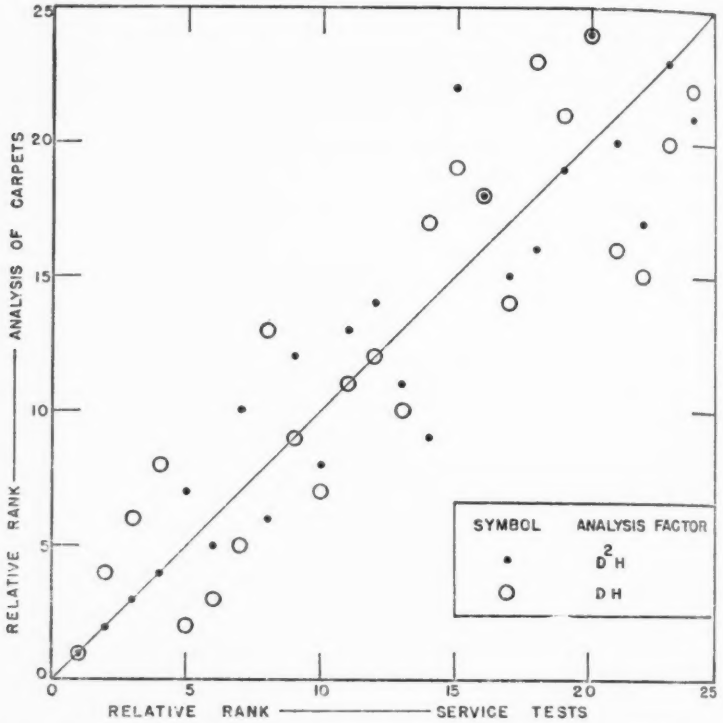


FIGURE 37.—*Relative rank of 24 carpets based upon the S indices of the service tests and the products of D^2H and DH, where D and H are density and height of pile, respectively.*

TABLE 5.—*Comparisons of results of tests of same carpets in different laboratories*

Laboratories	Machine	Ratio of results	Coefficient of variation
			Percent
NBS/*A*	NBS	[a] 1.59	18
NBS/*B*	do	[a] 1.23	28
NBS/*C*	do	[a] 2.18	47
NBS/*D*	Shawmut	[b] 1.09	20
NBS/*E*	do	[b] 1.18	21

[a] Ratio is based upon *S* indices.
[b] Ratio is based upon *E* indices.

The coefficient of variation is large for each machine and laboratory. One factor which probably contributes greatly to this variation is the variation in back thickness obtained for the same carpets in the different laboratories. Such a variation is critical since it affects the wear index directly and considerably. The difference in back thickness for the same carpet varied as much as 15 percent between laboratories. The large coefficient of variation of the ratios of the tests at the National Bureau of Standards to the tests at laboratory *C* with the NBS machine results from some factor which caused a large systematic difference in the results of the 10 velvet carpets. This fact is brought out by the different ratios obtained for the three weaves—namely, 1.77, 1.50, and 2.97 for the Wilton, Axminster, and velvet carpet series, respectively. The large ratios result because the *S* indices obtained in laboratory *C* were low owing to the extrapolation of the wear-test curves. Whether the much larger ratio for the velvet carpets is entirely due to extrapolation or whether it is due to another cause, such as a change in the leather, can not be determined from the available data.

The relationship of the results of the tests on the 24 carpets in the different laboratories and with the different machines to the results of the service tests for the three weaves is shown by the data given in table 6. This table contains the average and standard error of the ratios of the *S* indices of the service wear tests of carpets to those of the laboratory tests for the Wilton, Axminster, and velvet weaves. Since the *S* indices for the Shawmut machine were not obtained at laboratories *D* and *E*, the ratios given for this machine are based upon the *E* indices. The ratios for the tests with the Shawmut machine at the National Bureau of Standards are based upon both the *S* and *E* indices. The ratios for D^2H and DH are also given for comparison. The systematic difference between the results obtained at laboratory *C* and the other laboratories with the NBS machine is again very evident. The rather large discrepancies in the ratios for the different weaves obtained in each laboratory or for the same weave obtained in the different laboratories indicate the absolute need for closer standardization of the testing machines and procedures. The weighted averages of the different laboratories, with the one exception, are in good agreement for each testing machine. This good agreement merely indicates that the errors arising from nonuniform wear of the service wear tests, and due to variations in the laboratory wear tests and in the back thickness determinations, are compensated for in the weighted averages. It may be concluded that the results of adequately standardized laboratory wear tests can be used safely to judge the probable relative wear of carpets for the same use.

487101—42——5

TABLE 6.—*Average and standard error of the ratios of the S indices of the service wear of carpets to those of the laboratory for the Wilton, Axminster, and velvet weaves*

Weave	NBS machine				Shawmut machine				D^2H	DH
	NBS	Lab. *A*	Lab. *B*	Lab. *C*	NBS	NBS [a]	Lab. *D* [a]	Lab. *E* [a]		
Wilton	4.6 ±0.3	7.4 ±0.9	7.4 ±0.3	8.2 ±0.5	2.5 ±0.2	9.8 ±0.4	9.9 ±0.9	12.8 ±0.8	1.3 ±0.1	44 ±4
Axminister	7.8 ±0.8	4.2 ±1.7	6.9 ±1.0	11.4 ±1.1	2.7 ±0.3	13.3 ±1.8	14.3 ±0.5	14.1 ±1.0	1.5 ±0.2	23 ±2
Velvet	3.0 ±0.2	4.4 ±0.3	3.5 ±0.2	7.8 ±1.0	2.9 ±0.2	12.8 ±1.0	13.7 ±1.3	15.1 ±1.1	1.1 ±0.1	32 ±1
Weighted average	5.0	5.1	5.6	9.1	2.7	12.2	13.1	14.2	1.3	32

[a] These ratios are based upon the *S* indices of the service wear tests and the *E* indices of wear tests with the Shawmut machine.

6. EFFECT OF TYPE OF VACUUM-CLEANING SYSTEM ON THE SERVICE WEAR OF CARPETS

After the 24 carpets had been in service for nearly 2 years they were soiled in appearance and considerable dirt was embedded in the pile. Because of this condition, it seemed advisable to change the cleaning system and procedure. Since this might result in a change in the rate of wear of the carpets, it was decided to use three types of cleaners and to study the effect of each on the rate of wear. The three types of cleaners selected for this study were (I) suction combined with agitation and rotation of a brush, (II) suction, using the central suction system installed in the building, and (III) suction combined with rotation of a brush. Each cleaning system was adapted to utilize special paper bags for collecting the dirt which was removed from the carpets during each day's cleaning. A new paper bag, which had previously been weighed after being conditioned to 65-percent relative humidity and 70° F, was used each day. The duration of each daily cleaning was about 45 minutes on 900 ft.^{2} of carpet. The actual cleaning time was recorded for each day. The filled bags were again weighed after being conditioned to 65-percent relative humidity and 70° F., and the weight of the dirt collected each day was computed. The rate of wear of the carpets was determined by changes in the thickness of the pile.

The appearance of the carpets, after beginning the closely supervised cleaning on January 10, 1940, was definitely improved at the end of the first week. The type of cleaning had no measurable effect on the rate of wear of the carpets. Whether this would also be the case if similar experiments were conducted on new carpets cannot be determined from these tests.

The amount of dirt which is collected each day in experiments of this character depends upon a number of factors. It seems worth while to discuss the results more fully to aid those who may undertake similar experiments in the future.

The average amount of dirt collected per day for each of the 27 weeks of this investigation and the standard error of each average are given in table 7. The significance ratios of the difference between successive weeks are also given in the table, together with meteorological data on precipitation, sunshine, and remarks regarding number of days of rain, snow, sleet, and thawing.

The difference between the average amount of dirt collected per day during the first and the second week is highly significant. This difference cannot be attributed to abnormal weather conditions. It is unquestionably due to the removal of dirt which had accumulated in the pile of the carpets over a period of time. The difference between the total amount of dirt collected during the first and the second week is 3 pounds. It may be taken as an estimate of the amount of dirt which had accumulated in the pile of the carpets. On the basis of the daily average for the second week, this accumulated amount would represent approximately the quantity of dirt which is carried onto the carpets during 3 days of service wear. It explains the difference in appearance of the carpets before and after the beginning of the closely supervised cleaning. The cumulative daily amount of dirt removed during the first 4 weeks, Sundays excepted, is plotted in

TABLE 7.—*Results of tests with three vacuum-cleaning systems*

Type of cleaning	Week number	Daily average amount of dirt collected during week	Significance ratio of difference between consecutive weeks *	Precipitation	Sunshine	Remarks
		lb.		*Ins.*	*Percent*	
	1	1.45±.06		0.70	23	Sleet on 1 day; thawing on 4 days.
			**4.7			
	2	0.93±.09	0.0	.15	59	Snow on 2 days.
	3	.93±.06	.0	.91	80	Snow on 1 day, thawing on 6 days.
	4	.93±.08	.5	.08	58	Thawing on 6 days, rain on 1 day.
	5	.99±.08	.3	.27	50	Rain on 1 day.
I	6	1.03±.15		2.19	40	Snow on 1 day, sleet on 2 days, thawing on 3 days; rain on 3 days.
			1.7			
	7	0.76±.07		0.23	64	Snow on 1 day, sleet on 1 day, thawing on 1 day, rain on 1 day.
			0.2			
	8	.78±.06	*2.9	1.21	18	Rain on 5 days.
	9	.54±.06	1.3	0	64	
	10	.66±.08	0.8	1.73	50	Snow on 1 day, rain on 2 days.
	11	.59±.04	.3	0.48	58	Rain on 3 days.
	12	.58±.04	.2	2.33	45	Do.
	13	.59±.02		0.87	46	Snow on 1 day, sleet on 1 day, rain on 3 days.
			**4.0			
II	14	.75±.03	*2.4	2.99	15	Rain on 6 days.
	15	.58±.07	0.2	0	73	
	16	.56±.03	1.7	.45	46	Rain on 3 days.
	17	.46±.05	*2.0	.01	67	
	18	.59±.04	0.2	1.39	56	Rain on 1 day.
	19	.61±.09	.1	0.49	35	Rain on 4 days.
III	20	.60±.05	*2.0	.09	68	Rain on 1 day.
	21	.47±.04		0	41	
			1.2			
	22	.54±.03	1.9	.02	55	
	23	.63±.04	0.0	.70	55	Rain on 4 days.
	24	.63±.05	.3	2.39	56	Do.
I	25	.60±.06	*2.1	0.43	48	Rain on 2 days.
	26	.48±.02	1.3	.01	67	
	27	.53±.04		2.60	72	Rain on 1 day.

* Double and single asterisks indicate highly significant and significant ratios, respectively.

figure 38. The curve approaches a straight line after the first week. The slope of this straight line equals both the average amount of dirt deposited on the carpets each day and the average amount removed each day by the cleaning unit. The ordinate intercept, namely 3 pounds, represents the amount of accumulated dirt which was removed from the carpets by the cleaning unit during the first week and is in addition to the amount which was carried onto the carpets during this week and was also removed.

The random daily average fluctuations for the 27 weeks, table 7, are attributable to differences in weather conditions. For example, during the sixth week the precipitation was 2.19 inches; the snowfall was 2.7 inches; there was sleet on 2 days; and the sunshine was equal to 40 percent of the possible amount. On the other hand, during the seventh week the precipitation was 0.23 inch; the snowfall was 1.51 inches; there was sleet on 1 day; and the sunshine was equal to 64 percent of the possible amount. Similar differences may be noted between the eighth and ninth weeks, with 5 days of rain for a total precipitation of 1.21 inches and only 18 percent of sunshine during the eighth week compared with no precipitation and 65 percent of sunshine during the ninth week. It is apparent that there is a definite correlation between the amount of dirt deposited on the carpets and the weather conditions.

In addition to the random daily average fluctuations just referred to, systematic changes in the daily average may also be noted. These systematic changes are shown in figure 39, where the cumulative daily

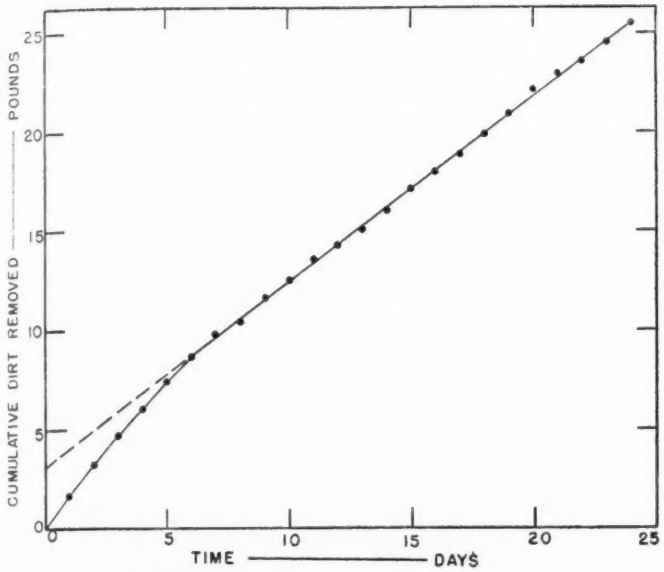


FIGURE 38.—*Cumulative amount of dirt removed from the carpets per day during 24 days of service wear.*

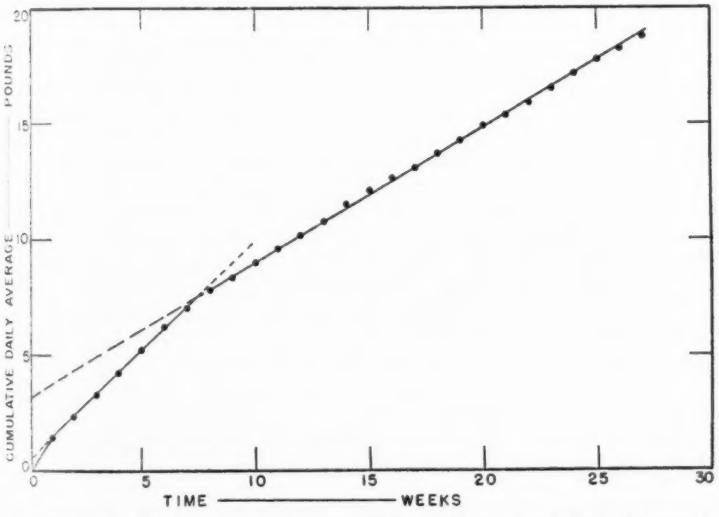


FIGURE 39.—*Cumulative daily average amount of dirt removed from the carpets per week during 27 weeks of service wear.*

average per week is plotted for the 27 weeks. The curve is comprised of three sections, each being represented by a straight line. The slope of each line represents the average amount of dirt deposited on the carpets each day. The reason for the change in the slope of the curve at the end of the first week has already been discussed. The change in the slope of the curve at the end of the seventh week is believed to be due to two factors, namely a seasonal change in weather and a substantial decrease in the traffic over the carpets. As a result of an executive reorganization, the number employed in the Procurement Division Building fell from 2,800 in January 1940 to 2,200 in June 1940, the maximum decrease being during March and April. This decrease lessened the traffic over the carpets in approximately the same proportion and had a pronounced effect on the amount of dirt deposited on the carpets. The approximate relationship between the amount of traffic over the carpets and the amount of dirt deposited on the carpets can be obtained by grouping the data for Saturdays, pay days, and regular weekdays. On Saturdays the traffic was found to be only 60 percent of that on a regular weekday, and the amount of dirt deposited on Saturdays averaged 75 percent of that on a regular weekday. On pay days the traffic was found to be 115 percent of that on a regular weekday, and the amount of dirt deposited on pay days averaged 115 percent on that on a regular weekday.

The fact that there is no change in the slope of the curve after the seventh week indicates that under close supervision the three systems of cleaning were equally effective. The dirt which had accumulated in the pile of the carpets prior to the close supervision in the use of the three cleaning systems is not attributable to the inadequacy of the cleaning system that was used but to the inadequate operation of the system.

7. NATURE OF WEAR OF THE FIBERS

Pile fibers of carpets which had been subjected to wear in service and on the NBS and Shawmut machines were examined microscopically. The wool fibers showed the same type of wear for the three conditions—namely, the fibers were frayed and split at the tip and some of them were fractured in one or more places where they had been repeatedly flexed. Spindle-shaped fibrils or cortical cells at the tips of the fibers and segments of fibers were broken off during each test. The particles shown in *A* of figure 40 are typical of the cortical cells and fiber segments that are worn off during a test. There was evidence of some cutting of the fibers that were taken from the carpet after 3 years of service wear. This cutting should be expected because the dirt which was removed by the vacuum-cleaning units contained numerous sand particles with sharp edges. Fibers that appear to have been cut in this manner are shown in *B* and *C* of figure 40.

Rayon and jute fibers, when used in the pile of carpets, seem to break off in short segments. There is no evidence of fraying at the tips of these fibers. A few rayon fiber segments are shown in *A* of figure 40.

8. CORRELATION OF WEAR TEST RESULTS WITH ANALYSIS OF CARPETS

The product of pile density squared and height of pile, D^2H, is plotted in figure 41 against the S index obtained with the NBS

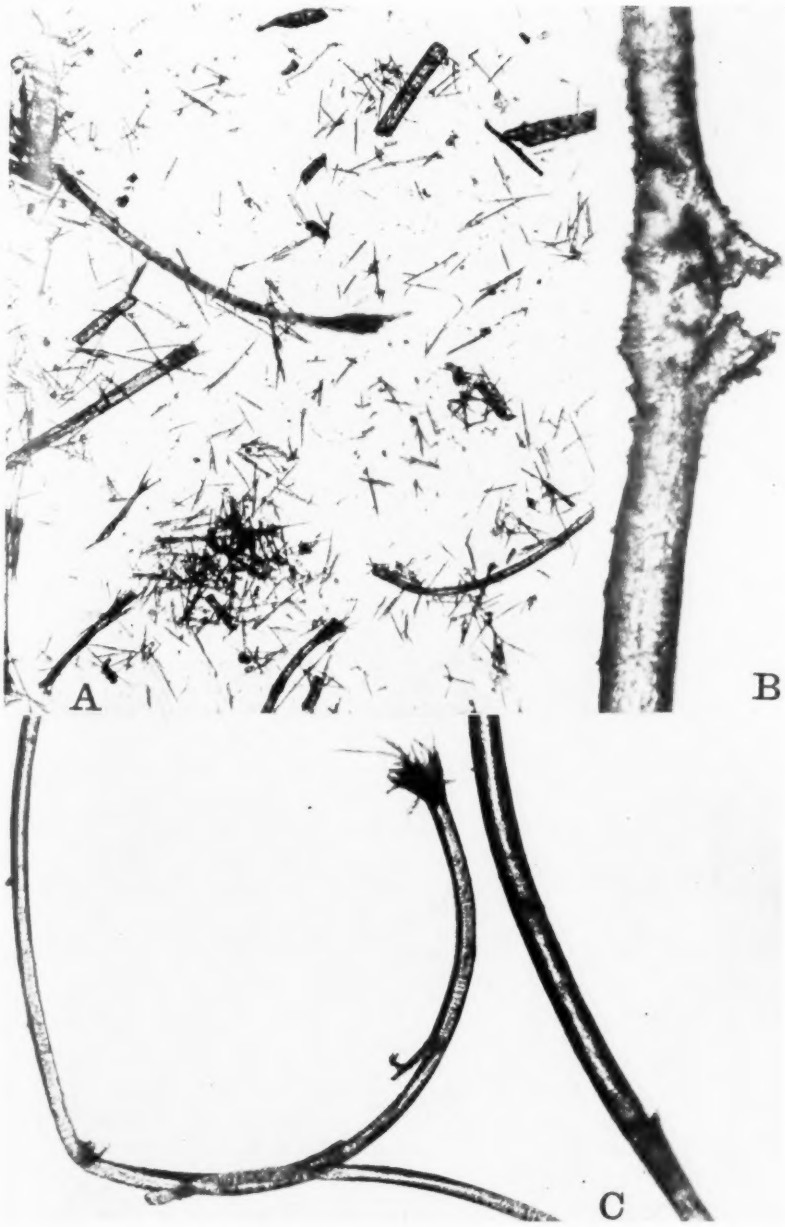


FIGURE 40.—*Nature of wear on fibers.*

A, Wool and rayon fibers worn on Shawmut machine. Magnification about ×50.
B, Wool fiber worn 3 years in the service test. Magnification about ×275.
C, Wool fiber worn 3 years in the service test. Magnification about ×100.

and Shawmut machines, respectively. The points belonging to the same series of carpets are connected by straight lines. It is apparent that the S index and D^2H for each series of carpets show in general a good linear correlation. However, such factors as weave, blend of wool, and nature of the pile affect the correlation

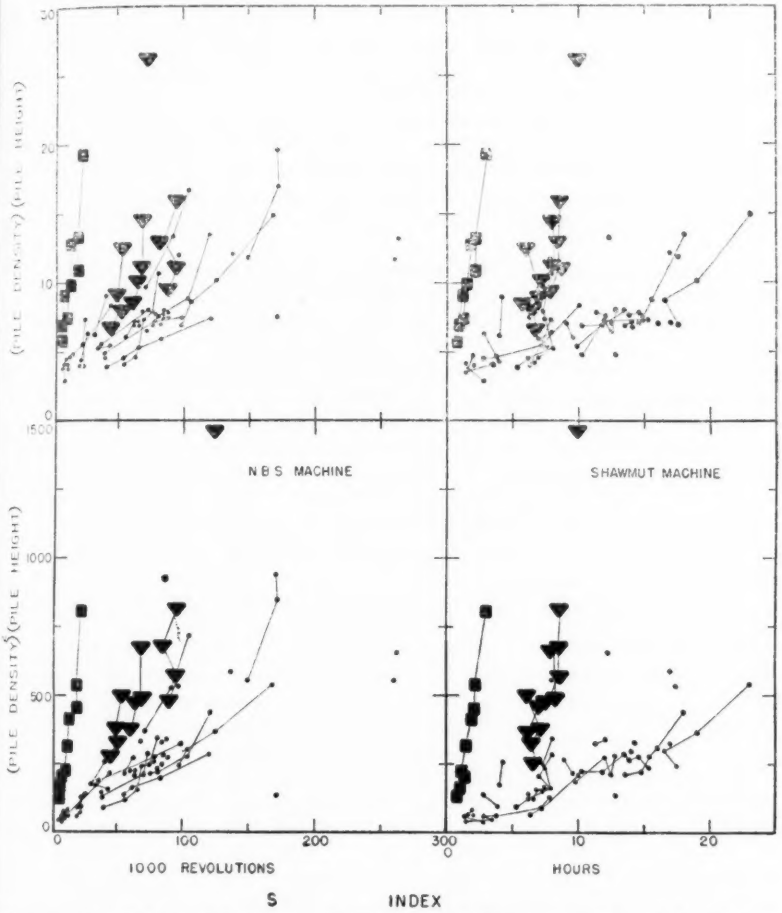


FIGURE 41.—*Relationship between the S indices of all carpets tested and the products of D^2H and DH, where D and H are density and height of pile, respectively.*

The chenille carpets are represented by the solid squares and the carpets containing highly twisted pile are represented by the solid triangles.

greatly. The chenille carpets are definitely isolated from the carpets of the other weaves. The very low wear indices for the chenille carpets were not expected because of the reputed long wear which chenille carpets give in service. The alkali-solubility of the wool forming the pile of these carpets was determined according to the method of Harris and Smith [8] and was found to be 80 percent for

[8] Milton Harris and Arthur L. Smith, *Oxidation of wool: Alkali-solubility test for determining the extent of oxidation*, J. Research NBS **17**, 577-583 (1936) RP928.

each carpet. Apparently the wool used in weaving these carpets was seriously damaged during processing. The very high alkali-solubility* explains fully the low wear indices which were obtained and also the separation of these carpets from the others in figure 41. The carpets in which the pile yarns are highly twisted also fall in a separate group. This separation is attributed to the process of setting the twist in the pile yarn. If the chenille carpets and those containing highly twisted pile yarn are eliminated, the remaining ones seem to fall in a fairly definite group, very much like that reported in Research Paper RP640. [9]

The product of the density of the pile and the height of the pile, DH, is also plotted in figure 41 against the S index obtained with the NBS and Shawmut machines, respectively. The points belonging to the same series of carpets are connected by straight lines. The correlations are in general the same as were just discussed for D^2H.

It may be concluded therefore that the constructional analysis of a carpet does not, in general, yield sufficient data to judge its probable wearability. It appears that the probable wearability can be obtained only by means of a standard wear test. The present wear tests must be very much more closely standardized before quantitative agreement in the results from different laboratories can be expected. Before this general standardization is attained, the results obtained in the different research laboratories, although not directly comparable, do furnish basic data regarding the effect of carpet construction on the wearability. The effect of systematic variations in carpet construction can be evaluated. Some of these effects are apparent from the several series of carpets which were tested.

The effects of systematic changes in the nominal construction of carpets on the S indices obtained with the NBS and Shawmut machines are given in tables 8 and 9. In general, a given percentage increase in the nominal number of tufts per square inch (table 8) results in a much greater increase in the S index than the same percentage increase in the nominal height of pile (table 9). This confirms in general the results published in Research Paper RP640. It is apparent that for a given increase in the nominal number of tufts per square inch the percentage increase in the wear index depends upon the height of the pile. Furthermore, the percentage increase in the S index varies with the weave. The same observations apply in general for a given increase in the nominal height of the pile. The extremely large percentage increase in the S index of the Axminster carpets with an increase in the nominal number of tufts per square inch results partly because of the decrease in the back thickness of the Axminster carpets having few rows per inch. No correction has been made in these tests for this decrease in back thickness of the Axminster carpets.

Another series of carpets which is of interest consists of six velvet carpets in which a stock-dyed standard base blend of the pile wool was combined with 20 percent of different wool wastes. The percentage changes in the S indices obtained with the NBS and Shawmut

[9] Herbert F. Schiefer and Richard S. Cleveland, *Wear of carpets*, BS J. Research **12**, 155–166 (1934) RP640.

*The alkali-solubility of the wool forming the pile of carpets of commercial production ordinarily does not exceed about 20 percent.

machines are given in table 10. The utilization of 20 percent of these respective wool wastes with the standard base blend had in general a beneficial rather than a detrimental effect on the *S* index.

TABLE 8.—*Effect of systematic changes in the nominal construction of carpets on the S indices*

[The increase in *S* index is computed for systematic increases in tufts per square inch, rows times pitch]

Nominal construction of carpets			Nominal increase in tufts per square inch	Increase in *S* index		
Wire height	Pitch per inch	Rows per inch		NBS machine	Shawmut machine	Service
WILTON						
Inch			*Percent*	*Percent*	*Percent*	*Percent*
0.145	8	8				
		10	25	65	26	
		12	50	154	58	
.172	8	8				
		10	25	46	22	
		12	50	98	57	
.145	9.5	8				
		10	25	100	18	50
		12	50	152	45	81
***CHENILLE**						
[a]0.625	10	5				
	12	6	44	100	57	
	14	7	96	317	200	
[a].75	10	5				
	12	6	44	109	50	
	14	7	96	185	110	
[a]1.00	10	5				
	12	6	44	102	46	
	14	7	96	275	131	
AXMINSTER						
[b]0.625	7	4.67				
		5.5	18	27	[c]−45	
		7.25	55	222	42	
		9	93	358	46	
[b].875	7	4.67				
		5.5	18	79	48	
		7.25	55	261	108	
		9	93	780	211	
[b].875	7	4				
		4.25	6	43	133	8
		4.5	12	57	87	23
		4.75	19	107	153	57
		6	50	475	380	134
		8	100	1,150	667	300
PLAIN VELVET						
0.18	7.25	8.8				
	8	8.8	10	30	30	
.22	7.25	8.8				
	8	8.8	10	29	12	
.28	7.25	8.8				
	8	8.8	10	22	23	
.41	7.25	8.8				
	8	8.8	10	39	28	
.187	8	6				
		7	17	33	17	54
		8	33	62	49	56
		9	50	103	32	103
		10	67	199	51	109

See footnotes at end of table.

TABLE 8.—*Effect of systematic changes in the nominal construction of carpets on the S indices*—Continued

Nominal construction of carpets			Nominal increase in tufts per square inch	Increase in *S* index		
Wire height	Pitch per inch	Rows per inch		NBS machine	Shawmut machine	Service
HARD TWIST VELVET						
Inch			*Percent*	*Percent*	*Percent*	*Percent*
0.145	7.67	7.5				
		8.5	13	41	[c]−9	
		9.5	27	104	13	
.192	7.67	7.5				
		8.5	13	32	13	
		9.5	27	90	30	
.246	7.67	7.5				
		8.5	13	38	16	
		9.5	27	75	18	
.299	7.67	7.5				
		8.5	13	28	33	
		9.5	27	79	41	
PRINTED VELVET						
0.25	8	7				
		9	29	111		
.37	8	7				
		9	29	86		
.44	8	7				
		9	29	64		

[a] This value is equal to the nominal length of the tuft or fur.
[b] This value is equal to the nominal length of the tuft or finish cut.
[c] A negative value indicates a decrease in *S* index.
* These chenille carpets were not typical of commercial production.

TABLE 9.—*Effect of systematic changes in the nominal construction of carpets on the S indices*

[The increase in *S* index is computed for systematic increases in wire height]

Nominal construction of carpets			Nominal increase in height of of pile	Increase in *S* index		
Rows per inch	Pitch per inch	Wire height		NBS machine	Shawmut machine	Service
WILTON						
		Inches	*Percent*	*Percent*	*Percent*	*Percent*
8	8	0.145				
		.172	19	25	[a]−4	
10	8	.145				
		.172	19	11	[a]−7	
12	8	.145				
		.172	19	[a]−3	[a]−6	
10	9.5	.145				
		.175	21	[a]−9	4	19
		.205	41	[a]−6	7	29

See footnotes at end of table.

TABLE 9.—*Effect of systematic changes in the nominal construction of carpets on the S indices*—Continued

Nominal construction of carpets			Nominal increase in height of pile	Increase in S index		
Rows per inch	Pitch per inch	Wire height		NBS machine	Shawmut machine	Service
				***CHENILLE**		
		Inches	*Percent*	*Percent*	*Percent*	*Percent*
5	10	[b].625				
		[b].75	22	19	43	
		[b]1.0	67	28	86	
6	12	[b]0.625				
		[b].75	22	24	36	
		[b]1.0	67	29	73	
7	14	[b]0.625				
		[b].75	22	[a]−5	0	
		[b]1.0	67	14	42	
				AXMINSTER		
4.67	7	[c]0.625				
		[c].875	42	4	[a]−51	
5.5	7	[c].625				
		[c].875	42	47	33	
7.25	7	[c].625				
		[c].875	42	17	[a]−28	
9	7	[c].625				
		[c].875	42	33	5	
6	7	[c].625				
		[c].875	42	1	13	33
		[c]1.125	83	6	23	93
				PLAIN VELVET		
8.8	7.25	0.18				
		.22	22	8	10	
		.28	56	37	15	
		.41	128	62	33	
8.8	8.0	.18				
		.22	22	8	[a]−6	
		.28	56	29	9	
		.41	128	74	31	
8	8	.125				
		.164	31	14	6	16
		.187	50	20	22	22
		.247	98	28	14	71
		.290	134	39	12	100
		.375	200	49	23	117
				HARD TWIST VELVET		
7.5	7.67	0.145				
		.192	32	16	[a]−6	
		.246	70	13	4	
		.290	100	24	[a]−10	
8.5	7.67	.145				
		.192	32	9	16	
		.246	70	11	32	
		.290	100	12	31	
9.5	7.67	.145				
		.192	32	8	8	
		.246	70	[a]−3	9	
		.290	100	8	12	
				PRINTED VELVET		
7	8	0.250				
		.370	48	30		
		.440	76	48		
9	8	.250				
		.370	48	15		
		.440	76	15		

[a] A negative value indicates a decrease in *S* index.
[b] This value is equal to the nominal length of the tuft or fur.
[c] This value is equal to the nominal length of the tuft or finish cut.
* These chenille carpets were not typical of commercial production.

TABLE 10.—*Effect of the admixture of various wool wastes with the standard base blend of the pile wool on the S index*

Composition of pile wool	Change in *S* index based upon the *S* index of the standard base blend	
	NBS machine	Shawmut machine
	Percent	*Percent*
Standard base blend plus 20 percent of dusted droppings	[a] −5	17
Standard base blend plus 20 percent of garnetted threads	36	42
Standard base blend plus 20 percent of blend through Schofield Picker	20	35
Standard base blend plus 20 percent of dusted droppings carded on breaker card	30	49
Standard base blend plus 20 percent of roving waste of base blend	32	32

[a] A negative value indicates a decrease in *S* index.

9. LIMITATIONS OF WEAR-TESTING MACHINES

The Shawmut machine was not found suitable for testing all pile-faced carpets. This was especially true for printed velvet carpets and for carpets where the pile yarn contained very little extractable oils. When these carpets were tested on the Shawmut machine, the wearing surface became excessively heated, apparently because of the higher friction between the wearing surface and the pile of the carpets. As the wearing surface became heated, the moisture content of the fibers was reduced and the friction between the pile and wearing surface was increased. This condition usually produced a shimmy motion between the wearing surface and the carpet specimen, and the fibers of the pile were pulled out in a short time. Figure 9 illustrates the general appearance of the specimen after such a test, and figure 42 shows the poor correlation which is obtained between the results of the NBS and Shawmut machines if the results of these tests are included. Intermittent operation of the Shawmut machine to minimize the amount of heating of the wearing surface or the use of a cooling device did not eliminate this type of wear. No difficulty was encountered in testing these carpets with the NBS machine, and no heating of the wearing surface was observed. The automatic adjustment of the speeds of the turntable and braking pulley relative to the driving pulley of the NBS machine, when the friction between the pile and the wearing surface is increased, prevents excessive generation of heat during the test. In this respect the friction drive of the NBS machine is preferable to the positive drive of the Shawmut machine.

The NBS machine has been found suitable for testing all types of pile-faced carpets. Probably the chief limitation of this machine has been the difficulty of obtaining a constant wearing surface. This difficulty has been overcome to a great degree by the specification for the leather and the procedure of preparing the wearing surface, which have been developed by Section IV on Pile Floor Coverings, of Subcommittee A–3, Committee D–13, ASTM. The matter of maintaining a constant wearing surface is still a serious problem and depends largely upon the care given to the machine by the operator. The inherent variation between different pieces of leather cannot be eliminated and ultimately may require the use of some other material for the wearing surface of this machine. The lack of uniform design of the NBS–type machines which are being used probably accounts

for some of the systematic differences in the results obtained in the interlaboratory tests.

The decrease in the back thickness of low-quality Axminster carpets during a test with the NBS machine presents a difficult problem for evaluating their relative wear resistances. Although this same condition was also encountered in the service tests of the low-quality Axminster carpets, further work needs to be done to obtain the correct solution. The lack of standardization of the NBS machine in the different laboratories can be rectified and uniform procedures for testing and for the evaluation of the wear index should be established

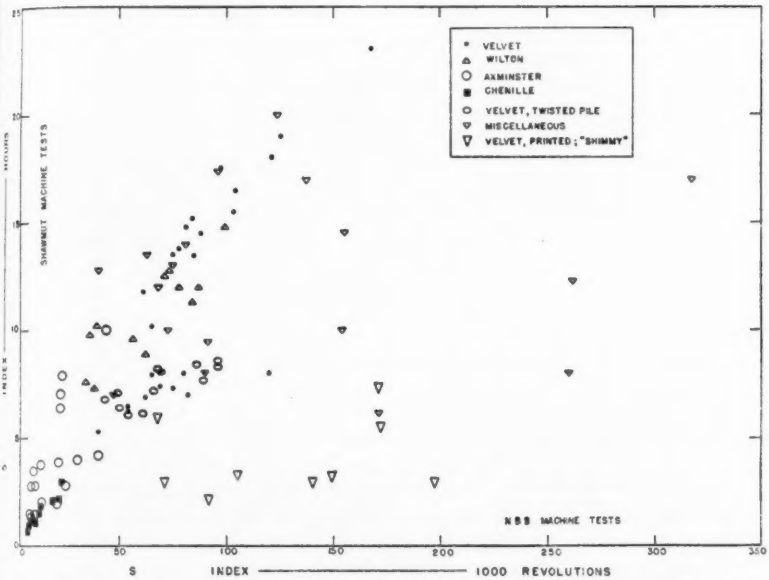


FIGURE 42.—*Relationship between the S indices of all carpets tested with the NBS and Shawmut machines.*

as soon as possible. The results presented in this paper should be of value in this standardization and unification of carpet wear testing.

VII. SUMMARY

The NBS and Shawmut machines for testing the wear resistance of carpets, a gage for measuring the thickness of carpets, and an instrument for measuring the length of a tuft of pile from a carpet are described.

The results of the tests with the NBS machine depend upon the downward force at each pulley, the braking torque, the speed of the turntable, the height of the nozzle above the pile, the amount of suction at the nozzle, and the relative humidity and temperature of the air in which the tests are made. These factors must be maintained constant in order to effect standardization of the wear test and to obtain quantitative agreement in the results between different laboratories.

The S index, which is the time required to wear the pile of a carpet down to one-fourth of the matted pile thickness, is more reliable than the K and E indices, and in the service tests it corresponded more nearly with the time at which a carpet would be discarded on account of visible wear. The deviation of the S index of a single test from the average is less than 10 percent in 9 trials out of 10.

The correlation of the results obtained during the 3 years of severe wear in service on 24 carpets of Axminster, velvet, and Wilton weaves with the results obtained with the NBS and Shawmut machines on the same carpets and with the analysis of the carpets is good for each weave. However, the ratio of the results of service wear to the results of machine wear or to the carpet analysis is different for each weave. This variation is attributed primarily to changes of wool blend, dyeing, and yarn structure between the carpets of the three weaves.

The increase in S index of the service tests for a given percentage increase in pile density is about three times as great as that which results from the same percentage increase in pile height.

The relative rank of 24 carpets which were tested on the NBS and Shawmut machines in different laboratories correlated well with the relative rank determined by the service tests. The ratios of the service wear results to the results obtained in the different laboratories show systematic differences between weaves and between laboratories, expecially those ratios obtained with the NBS-type machine. The latter difference is attributed primarily to a lack of uniformity in the testing procedures. The results of adequately standardized laboratory wear tests can be used safely, however, to judge the probable relative wear of carpets for the same use.

The type of vacuum cleaning had no measurable effect on the rate of wear of the carpets in the service tests. The amount of dirt deposited on the carpets per day during the service tests varied directly with the number of people walking over the carpets and with seasonal changes in the weather. Under close supervision, the three systems of vacuum cleaning were equally effective.

The same type of wear on the wool fibers was observed in the service, NBS, and Shawmut machine wear tests. The fibers were frayed and split at the tip and some of them were fractured in one or more places. Spindle-shaped fibrils or cortical cells were broken off at the tips of the fibers or segments of fibers were broken off. Some of the fibers were partially cut by the sharp edges of sand particles which were deposited in the pile during the service tests. Jute and rayon pile fibers seem to break off in short segments during a wear test, with no fraying at the tips of the fibers.

The correlation between the results of wear tests and the constructional analyses of carpets depends upon such factors as weave, blend of wool, dyeing, chemical degradation of the wool, and twist of the pile yarn. The constructional analysis of a carpet does not yield sufficient data in general to judge the probable wearability of the carpet.

A given increase in the nominal number of tufts per square inch, density of pile, increases the S index very much more than the same percentage increase in nominal height of pile and confirms the results published in NBS Research Paper RP640. The increase in S index of a carpet for a given increase in pile height and pile density varies with the type of wear test and also with weave and pile construction.

The author expresses his appreciation to A. G. Ashcroft, J. N. Dow, G. E. Hopkins, L. R. Jones, and A. G. Mann for their interest and suggestions during this investigation. The assistance of the Alexander Smith & Sons Carpet Co., the Bigelow Sanford Carpet Co., the Mohawk Carpet Mills, Inc., the United States Testing Co., the Hoover Co., the Westinghouse Electric & Mfg. Co., the Shawmut Engineering Co., and the Procurement Division of the United States Treasury Department is gratefully acknowledged.

WASHINGTON, September 18, 1942.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1506

Part of Journal of Research of the National Bureau of Standards, Volume 29, November 1942

CHEMICALLY MODIFIED WOOLS OF ENHANCED STABILITY

By Walton B. Geiger, F. F. Kobayashi, and Milton Harris[1]

ABSTRACT

Recent work at this Bureau has shown that the disulfide cross-linkages of wool can be transformed to more stable *bis*-thioether linkages by a two-step process. The disulfide groups are first reduced to sulfhydryl groups by means of a mercaptan, and then, by treating the wool with an aliphatic dihalide, pairs of sulfur atoms are linked together through short hydrocarbon chains. Wools modified by such a process have now been studied more extensively. It was found that they are decidedly more stable than untreated wool toward many chemical agents, including alkalies, acids, oxidizing agents, and reducing agents; are stained less easily by metals; and are attacked much less readily by certain biological agents, including moths, carpet beetles, and enzymes.

CONTENTS

	Page
I. Introduction	381
II. Experimental procedure	382
1. Materials	382
2. Methods	382
(a) Reduction	382
(b) Alkylation	383
(c) Analysis	383
III. Results and discussion	384
1. Resistance to alkali	384
2. Resistance to acids	385
3. Resistance to reducing agents	386
4. Resistance to oxidizing agents	386
5. Resistance to staining by heavy metals	387
6. Resistance to enzymes, moths, and carpet beetles	387
IV. References	389

I. INTRODUCTION

One of the greatest practical disadvantages of wool has been that it is only moderately stable to a number of chemical agents, especially those that primarily attack the disulfide group of the cystine of the wool. For example, the degradation of wool by alkalies [1],[2] by oxidizing agents such as peroxide [2] or chlorine [3], or by reducing agents such as the bisulfites or dithionites[3] [4], has been shown to result in part at least from the breakdown of these groups. Damage to wool

[1] Research Associates at the National Bureau of Standards, representing the Textile Foundation.
[2] Figures in brackets indicate the literature references at the end of this paper.
[3] Also termed "hydrosulfites" or "hyposulfites."

487101—42——6

by light also involves the breakdown of disulfide groups [5]. In addition, rupture of these groups seems to be involved when moths attack wool [6], and also is necessary before enzymes can digest it [7]. Yet disulfide groups are of primary importance in maintaining the unusual mechanical properties of wool, particularly its elasticity [8], since they serve as cross-links between the peptide chains of the wool protein [9]. For these reasons there would seem to be an obvious advantage in transforming the disulfide groups to more stable ones through a process not deleterious to the mechanical properties of the wool.

Recent work at this Bureau [9] has led to the development of a series of chemical reactions by which this can be done. By treating the wool with a solution of thioglycolic acid or other mercaptan at a pH below 7.0, a portion of its disulfide groups can be reduced to sulfhydryl groups without destroying its fibrous structure, and without detectable changes in other chemical linkages. This reaction may be represented as follows:

$$W-S-S-W+2HSCH_2COOH \longrightarrow 2W-SH+ \begin{matrix} S-CH_2COOH \\ | \\ S-CH_2COOH \end{matrix} \quad (1)$$

where W represents the portions of the wool connected by the disulfide groups. By treating the reduced wool with an alkyl dihalide, the sulfur atoms can be linked through short hydrocarbon chains, and new cross-links that are much more stable than the disulfide groups are produced, as the following equation indicates:

$$2W-SH+(CH_2)_nX_2 \longrightarrow W-S-(CH_2)_n-S-W+2HX, \quad (2)$$

where X represents a halogen atom.

Work already published [9] has demonstrated that wools containing cross-links of this sort possess enhanced stability to alkali. Since then a greater variety of products has been prepared, and their stability to moths, molds, and enzymes, has been studied. In addition, a number of improvements in the process for preparing such modified wools have been made and are described below.

II. EXPERIMENTAL PROCEDURE

1. MATERIALS

The yarn used in the present study was part of the lot used in earlier investigations [7, 9]. This yarn was a four-ply worsted prepared from raw wool that had been previously extracted with Stoddard solvent and washed with water. The yarn was further purified by extraction with alcohol and with ether for 6 hours each in a modified Soxhlet apparatus, so constructed that neither hot solvent nor vapor should come in contact with the wool, and finally by washing with distilled water. The cloth used was a plain-woven worsted of the type described in Commercial Standard CS65–36 [10].

2. METHODS

(a) REDUCTION

Wool can be reduced, not only with sodium thioglycolate, as in the earlier work [9], but also with other salts of this acid, with the free acid, or with other mercaptans. Comparison of the results obtained with a

number of the salts of thioglycolic acid showed that the calcium salt offered unusual advantages, since the products had the best tactile properties, and possessed the greatest stability toward alkali of any studied.

The reduction was carried out by immersing the wool in a solution of calcium thioglycolate at 50° C and at pH 5. Under these conditions, reduction was complete in 2 hours, while 20 hours was required for reduction by the older procedure. To reduce about one-sixth of the cystine, 50 ml of a 0.02 *N* solution of calcium thioglycolate was used for each gram of wool. To reduce about one-half of the cystine, 20 ml of a 0.3 *N* solution was used for each gram of wool. To obtain products in which two-thirds of the cystine had been reduced, two applications of this latter reduction process were required. Products in which five-sixths of the cystine had been reduced were prepared by applying this reduction process four times. When successive reductions were used, each reduction was followed by alkylation.

(b) ALKYLATION

Immediately after reduction, the wool was washed with water, then with 0.01 *N* phosphate buffer at pH 8.0, and again with water. The wool was then immersed in a 0.1 *M* solution of phosphate buffer at pH 8.0 and 50° C, in which the alkylating agent had been suspended with the aid of a cationic wetting agent. About 0.0005 mole of the alkylating agent and 20 ml of the buffer were used for each gram of wool. The nitroprusside test given by the sulfhydryl groups of the reduced wool ordinarily became negative within 1 hour, but as a precaution the alkylations were continued for a total of 2 hours.

An investigation of the usefulness of a large group of organic dihalides as alkylating agents showed that they may be grouped roughly into three classes. The first class may be termed satisfactory reagents (those which react with reasonable rapidity and yield very stable products) including methylene bromide, trimethylene bromide, tetramethylene bromide, and 1,4-dichlorobutene-2. The second class consists of fair reagents (which react more slowly but yield satisfactory products) such as trimethylene chloride, triglycol dichloride, or *bis*-2-chloroethoxymethane. The third class includes unsatisfactory reagents, such as certain dihalides that are easily hydrolyzed, as benzal chloride and dichloroacetic acid, others with only one sufficiently reactive halogen atom, such as ethylene bromide, 1,3-dichloropropanol-2, and 2,2′-dichlorodiethyl ether, and others that produce side reactions, such as styrene dibromide or 1,3-dibromopropanol-2, which may act as oxidizing agents, since the sulfhydryl groups are rapidly converted to the disulfide stage. The results described in this paper are mainly those obtained with one of the best reagents, trimethylene bromide.

(c) ANALYSIS

The amount of unchanged cystine in the modified wools was determined by the method of Sullivan [11]. The concentration of the solutions of thioglycolic acid was measured by titrating a sample with a 0.05 *N* solution of iodine, using starch as an indicator. The sulfur analyses were made by the oxygen-bomb method [12]. The alkali-solubility was determined by the method of Smith and Harris [2] and represents the percentage of the wool dissolved in 1 hour by 100 times its weight of a 0.1 *N* solution of sodium hydroxide at 65° C.

The breaking strengths of the samples of cloth were determined in the warp direction with a pendulum-type machine by the raveled-strip method [10], and each value represents the average of at least 10 measurements. The reflectances of the samples of cloth were measured by the method of Reimann and Mease [13].

III. RESULTS AND DISCUSSION

1. RESISTANCE TO ALKALI

Wool frequently comes in contact with alkali in processes like laundering and scouring. The action of alkali may diminish the strength and durability of the wool, cause it to turn yellow, and impair its tactile properties, rendering it harsh. Since the linkages of wool protein most susceptible to disruption by alkali are the disulfide groups, transforming them to the more stable *bis*-thioether groups should increase the stability of the wool to alkali. The effect of boiling with dilute alkali on untreated wool and on a modified wool is illustrated by the photomicrographs of fibers in figure 1. It is apparent that the fibers of the untreated wool show far more swelling and disruption than do the fibers of the modified wool.

TABLE 1.—*Action of alkalies on the untreated wool and on the modified wools prepared by reduction, followed by alkylation with* $(CH_2)_3Br_2$

[Alkali-solubility of the wools, and their reflectance and breaking strength after boiling them for 1 hour with 0.02 *N* sodium carbonate]

Cystine	Alkali-solubility	Reflectance [a]	Breaking strength [b]	
			Before treatment with Na_2CO_3	After treatment with Na_2CO_3
UNTREATED				
Percent 12.2	*Percent* 10.0	*Percent* 37.8	*kg* 14.0	*kg* 10.0
MODIFIED				
10.0	6.2	37.6	13.5	11.5
6.5	2.9	41.0	13.5	12.0
4.0	2.5	46.5	12.5	12.0
2.0	2.0	47.5	12.5	11.5

[a] With respect to MgO.
[b] Strips 2.54 cm wide, 49 ends.

Three other tests for resistance to alkali were also used: (1) alkali solubility, (2) the extent of yellowing of the products by alkali, and (3) the effect of alkali on the breaking strength of strips of cloth. The alkali-solubilities given in table 1 show that the modified wools have a decidedly greater resistance than does untreated wool. Closer examination of these data also shows that, although the resistance to alkali increased as the cystine content decreased, little advantage was gained by diminishing the cystine content below 6 percent. Treatment with boiling solutions of sodium carbonate, which rapidly turns untreated wool yellow, has considerably less effect upon the modified wools, as the reflectance data of table 1 indicate. The loss in reflectance upon treatment with alkali became less as the content of un-

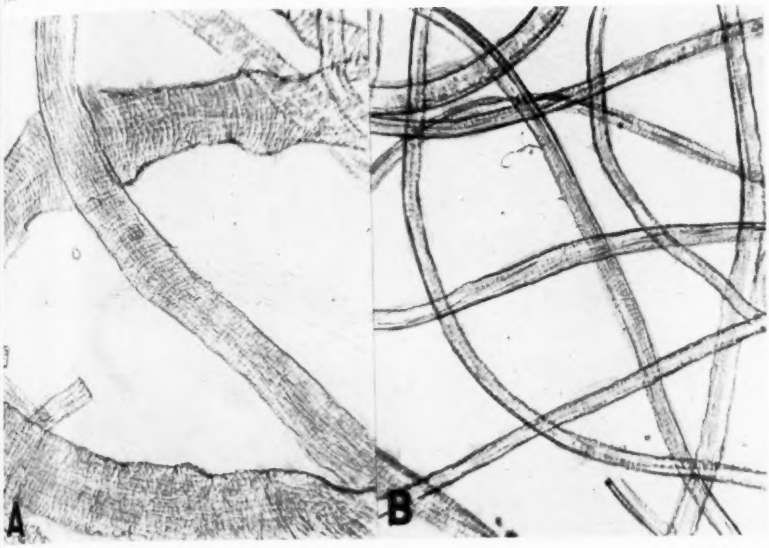


FIGURE 1.—*Wool fibers after treatment for 30 minutes at 100° C with 0.01 N* NaOH.

A, untreated wool; *B*, modified wool (cystine content, 6.5 percent) prepared by reduction with calcium thioglycolate and alkylation with $(CH_2)_3Br_2$. Magnification ×150.

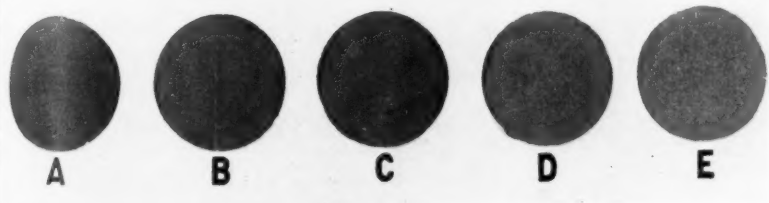


FIGURE 2.—*Wool samples after treatment for 30 minutes at 100° C with 0.02 N lead acetate,* pH 5.0.

Untreated wool, *A*; modified wools prepared by reduction with calcium thioglycolate and alkylation with $(CH_2)_3Br_2$; *B*, 10.6% cystine; *C*, 6.5% cystine; *D*, 4.6% cystine; *E*, 2.6% cystine.

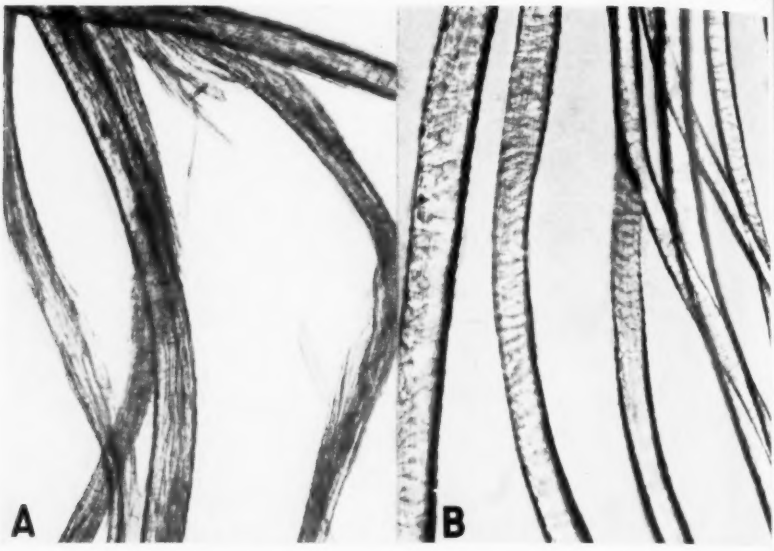


FIGURE 3.—*Wool fibers after treatment with pepsin for 2 weeks* [7].

A, Untreated wool; *B*, modified wool (cystine content, 6.5%) prepared by reduction with calcium thioglycolate and followed by alkylation with $(CH_2)_3Br_2$. Magnification ×150.

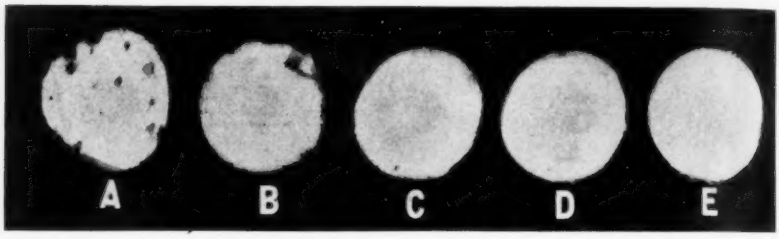


FIGURE 4.—*Wool samples after subjection to moth larvae.*

Untreated wool, *A*; modified wools prepared by reduction with calcium thioglycolate and followed by alkylation with $(CH_2)_3Br_2$; *B*, 10.0% cystine; *C*, 6.5% cystine; *D*, 4.0% cystine; *E*, 2.0% cystine.

FIGURE 5.—*Wool samples after subjection to the larvae of black carpet beetles (Attagenus piceus).*

Untreated wool, *A*; modified wools prepared by reduction with calcium thioglycolate followed by alkylation with $(CH_2)_3Br_2$; *B*, 10.0% cystine; *C*, 6.5% cystine; *D*, 4.0% cystine; *E*, 2.0% cystine.

changed cystine was diminished. The effect of treatment with boiling solutions of sodium carbonate upon the breaking strengths of strips of wool cloth is also reported in table 1. The loss in breaking strength of the chemically modified wools upon treatment with sodium carbonate was somewhat less than that of the untreated wool.

2. RESISTANCE TO ACIDS

Not only do the modified wools show improved stability to alkali alone, but they also show greater stability to alkali after being treated with acids. Improved stabi ity to such a succession of treatments is important because degradation, which may occur when wool is carbonized, acid-dyed, or acid-fulled, may be greatly accentuated when the material later comes in contact with alkali, as in laundering. Table 2 gives typical results. Because the amounts of soluble nitrogenous materials, which represent partly hydrolyzed protein fragments, that result from each acid treatment are similar for the untreated and the modified wool, it seems likely that about as many peptide chains are hydrolyzed by the acid in one material as in the other, since there is no *a priori* reason for peptide bonds to be stabilized by a reaction involving only the sulfur. The hydrolytic action of a given acid treatment should therefore result in about the same decrease in average molecular weight for each material. The subsequent alkali-solubility test involves breakdown of the disulfide groups of the unmodified wool but not of the *bis*-thioether groups of the modified wool. For these reasons the greater alkali-solubility of the unmodified wool appears to depend on a decrease in molecular weight that results from the rupture both of disulfide cross-links and of peptide bonds.

TABLE 2.—*Action of acids on untreated wool and on modified wool (cystine content 6.5%) prepared by reduction, followed by alkylation with* $(CH_2)_3Br_2$

Wool	Conditions	Alkali-solubility—		Nitrogen liberated in percentage of total Nitrogen
		Before treatment	After treatment	
		Percent	*Percent*	
Untreated	HCl, 0.1 *N*, 65° C, 24 hours	9.5	20.0	2.0
Modified		2.5	6.3	1.7
Untreated	HCl, 0.1 *N*, 65° C, 10 days	9.5	80.0	11.8
Modified		2.5	45.0	11.3
Untreated	H_2SO_4, 0.1 *N*, 65° C, 24 hours	9.5	28.8	2.9
Modified		2.5	9.9	2.5

The carbonizing of wool with sulfuric acid differs from the above treatments in involving baking at a high temperature (about 125° C). The results obtained on subjecting the untreated and the modified wool to a typical commercial carbonizing process are recorded in table 3. The untreated wool, after carbonizing, had a high alkali-solubility, so damage might easily result from laundering or other treatments involving alkali. The alkali-solubility of the modified wool after carbonizing had increased too, but the final value was much lower.

TABLE 3.—*Effect of carbonizing with sulfuric acid on the untreated wool, and on the modified wool (cystine content 6.5%) prepared by reduction, followed by alkylation with* $(CH_2)_3Br_2$

Wool	Alkali-solubility—		Breaking strength [a]—	
	Before carbonizing	After carbonizing	Before carbonizing	After carbonizing
	Percent	*Percent*	*kg*	*kg*
Untreated	9.5	19.4	13.5	13.5
Modified	3.5	11.0	13.0	13.0

[a] 2.54 cm strips, 49 ends.

3. RESISTANCE TO REDUCING AGENTS

Wool is often subjected to the action of reducing agents. For example, wool papermakers' felts frequently come in contact with sulfites. Reducing agents, including dithionites and formaldehyde-sulfoxylates, are used with wool as stripping agents, and dithionites are also used in dyeing wool with indigoid colors. Such reducing agents tend to make wool extremely susceptible to the action of alkali [4]. Reducing agents appear to attack wool mainly by breaking the disulfide linkages of the cystine. Sodium bisulfite, for example, probably reacts as follows [14]:

$$W-S-S-W+NaHSO_3 \longrightarrow W-S-SO_3Na+W-SH.$$

The ionized thiosulfate and mercaptan groups formed by this reaction would be expected to increase the alkali-solubility of the wool. The *bis*-thioether linkages of the modified wools cannot, however, react in this way, so such wools should be far more stable to reducing agents. The results obtained by determining the alkali-solubility of samples of unmodified and modified wool that had previously been treated with reducing agents are recorded in table 4. The modified wool was found in every case to be considerably less affected by the reducing treatment than was the untreated wool.

TABLE 4.—*Action of the reducing agents on the untreated wool and on the modified wool (cystine content, 6.5 percent) prepared by reduction, followed by alkylation with* $(CH_2)_3Br_2$

[For each gram of wool, 100 ml of the indicated reagent was used]

Reagent	Conditions	Alkali-solubility of—	
		Untreated wool	Modified wool
		Percent	*Percent*
None		10.0	2.5
$NaHSO_3$	1%; 100°C; 1 hour	15.2	4.8
$Na_2S_2O_4$	10%; 50°C; 2 hours	39.0	4.5
$NaSO_2-CH_2O$	5% 50°C; 2 hours	13.3	3.7
NaSH	0.2 *N* 50°C; 2 hours	41.5	3.2

4. RESISTANCE TO OXIDIZING AGENTS

Wool comes in contact with oxidizing agents during bleaching with peroxide, during treatment with chlorine, and also in use, through the action of light and air. The effect on wool of certain chemical

oxidizing agents is recorded in table 5, where alkali-solubility is again used as a criterion of damage by the oxidizing agents. The results show that the transformation of disulfide groupings to *bis*-thioether groupings diminishes the deleterious effects of oxidizing agents, since, although the alkali-solubilities of both the modified and the untreated wool have increased, those of the modified wool remain low enough to indicate considerable resistance.

TABLE 5.—*Action of oxidizing agents upon untreated wool, and upon modified wool (cystine content, 6.5 percent) prepared by reduction, followed by alkylation with* $(CH_2)_3Br_2$

[For each gram of wool, 100 ml of the indicated reagent was used]

Reagent	Conditions	Alkali-solubility of—	
		Untreated wool	Modified wool
		Percent	*Percent*
None		10.0	2.5
Cl_2	0.01 *N*; 100°C; 1 hour	13.6	6.6
H_2O_2	2 vol; 50°C; 1 hour	15.5	4.0
$KMnO_4$	1%, 35°C; 1 minute	17.5	10.4
$K_2Cr_2O_7$	0.2%; 100°C; 1 hour	11.0	4.6

5. RESISTANCE TO STAINING BY HEAVY METALS

Wool is easily stained by contact with metals, as by the metal fasteners sometimes used with wool clothing. This staining may possibly result either directly from the reaction of the wool with the metal or from the reaction with oxides or salts formed on the surface of the metal. It was found qualitatively that the extent of staining by solutions of certain salts of iron, silver, copper, and lead was considerably greater with the untreated wool than with certain of the modified wools. The results obtained by staining with lead acetate are illustrated in figure 2. The modified wools were stained very much less by a solution of lead acetate than was the untreated wool, and the extent of staining decreased as the amount of the unchanged cystine decreased. Most of the modified wools studied were similar in this respect, but wool prepared by reduction followed by alkylation with methylene bromide, a process that converts its cystine to djenkolic acid (which contains -S-CH_2-S- linkages), was found to be exceptional, since it was stained by lead acetate almost as readily as untreated wool.

6. RESISTANCE TO ENZYMES, MOTHS, AND CARPET BEETLES

Proteolytic enzymes digest wool extensively only after a portion of the disulfide bonds have been broken, although less complete digestion takes place after mechanical injury or after contact with dilute acid for several days [7]. The wools containing *bis*-thioether cross-linkages showed greatly enhanced resistance to digestion, and were not attacked by pepsin even after mechanical injury, or after treatments with acid sufficient to render untreated wool readily digestible. Photomicrographs illustrating the experimental results are shown in figure 3.

Moth larvae, according to Linderstrøm-Lang [6], can digest wool only after breaking its disulfide cross-linkages by the action of a

reducing agent present in their intestinal tracts. For this reason it seemed probable that the modified wools containing *bis*-thioether linkages would be far more stable to biological agents than untreated wool, and such stability was actually observed. The new linkages probably interfere with the preliminary reductive step, since *bis*-thioether linkages, as shown above, are very resistant to the action of reducing agents.

A study of the ability of the new cross-linkages to minimize the extent of attack by moths has shown that the modified wools are attacked to a considerably less extent than is untreated wool, and that the resistance increases as the content of unchanged cystine decreases. Table 6 gives the results obtained after the wool samples had been subjected to the action of moth larvae, and the samples are shown in figure 4.[4] The modified materials having cystine contents of 6 percent or less were only slightly attacked, and this attack was mainly around the edges, whereas numerous holes were eaten in the untreated samples. It also appears that reducing the cystine content to 6 percent provides about as much protection as the more extensive treatments. It should be pointed out that the mothproofness produced by the present method is not removed by laundering or dry cleaning, since it is "built into" the molecule as an integral part of its chemical structure.

TABLE 6.—*Action of moth larvae upon untreated and upon chemically modified wools prepared by reduction followed by alkylation with* $(CH_2)_3Br_2$

[Ten larvae were used for each sample.]

Type	Cystine content	Loss in weight
	Percent	*Percent*
Untreated wool	12.2	15.5
Modified wool	10.0	8.0
Do	6.5	.3
Do	4.0	2.9
Do	2.0	.1

TABLE 7.—*Action of larvae of the black carpet beetle on the untreated and on the modified wools prepared by reduction and followed by alkylation with* $(CH_2)_3Br_2$

[Each sample was exposed to 10 larvae for 30 days.]

Type	Cystine content	Weight of excrement
	Percent	*mg*
Untreated wool	12.2	52
Modified wool	10.0	45
Do	6.5	21
Do	4.0	34
Do	2.0	23

Carpet beetles were found to damage both the untreated and the modified wools more extensively than did moth larvae, as table 7 and figure 5 illustrate. Nevertheless, the modified wools were decidedly more resistant than the untreated wool to such attack.

[4] We thank John A. Levering and J. W. Creely, of the Eavenson & Levering Co., Camden, N. J., for the tests with moth larvae, and A. G. Ashcroft and R. C. Allison, of Alexander Smith & Sons Carpet Co. Yonkers, N. Y., for the tests with carpet beetles.

IV. REFERENCES

[1] J. A. Crowder and M. Harris, J. Research NBS **16,** 475 (1936) RP885.
[2] A. L. Smith and M. Harris, J. Research NBS **16,** 301 (1936) RP875.
[3] J. A. Crowder and M. Harris, J. Research NBS **17,** 577 (1936) RP928.
[4] C. S. Lowe, A. C. Lloyd, and A. C. Smith, Am. Dyestuff Reptr. **30,** 81 (1941).
[5] H. A. Rutherford and M. Harris, J. Research NBS **20,** 559 (1938) RP1090.
[6] K. Linderstrøm-Lang and F. Duspiva, Z. physiol. Chem. **237,** 131 (1935).
[7] W. B. Geiger, W. I. Patterson, L. R. Mizell, and M. Harris, J. Research NBS **27,** 459 (1941) RP1433.
[8] M. Harris, L. R. Mizell, and L. Fourt, J. Research NBS **29,** 73 (1942) RP1486.
[9] W. I. Patterson, W. B. Geiger, L. R. Mizell, and M. Harris, J. Research NBS **27,** 89 (1941) RP1405.
[10] NBS Commercial Standard CS59–36 (1936).
[11] M. X. Sullivan, Public Health Reports 86 (1930).
[12] R. T. Mease, J. Research NBS **13,** 617 (1934) RP731.
[13] G. B. Reimann and R. T. Mease, NBS Letter Circular LC617 (Nov. 8, 1940).
[14] F. F. Elsworth and H. Phillips, Biochem. J. **35,** 135 (1941).

WASHINGTON, June 3, 1942.